Electron Probability Distribution in AIM and ELF Basins

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Abstract: The probabilities of finding a certain number of electrons enclosed in a given volume is calculated and discussed for a series of molecules. Two different methodologies to do the partition of the molecular space in separate volumes are investigated: the Atoms in the Molecules, AIM, topologic analysis of the density, and the topologic analysis of the Electron Localization Function (ELF). The formulas to calculate the probability distribution are reviewed and the way to implement them shortly explained. For a series of molecules, we present how the probability distribution complement the chemical information about the localization of the electrons in certain regions of the space. The calculations show that the probability of finding Z electrons in the AIM atomic basin associated to an atom of atomic number Z is, in general, low, even when the average number of electrons is close to Z. The probability distribution on the ELF basins associated to bonds yields new insight about the nature of the respective bond.

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Introduction

Quantum mechanics does not give sharp boundaries for the regions in which electrons move in a molecule or crystal. In fact, there is no perfect localization of an electron in a region of the space. However, the concepts of electron pairs and bonding are firmly rooted in the models of the chemistry. Therefore, it has been for a long time a matter of research to find simple and clear ways of separating the space in regions with a chemical and physical meaning. The loge theory of Daudel,[1] the atoms in molecules (AIM) model of Bader,[2] and the Electron Localization Function (ELF)[3] are examples of this. Once the space is divided in various regions defining nonoverlapping volumes one can ask for the average number of electrons enclosed in each volume. For instance, one expects to find on average two electrons associated with a region of the space where the models of chemistry put an electron lone pair. Because the operator that counts the number of electrons in a given volume does not commute with the hamiltonian of the system it cannot be an observable, and one should use average numbers, fluctuations,[2] and probabilities. The probabilities of finding certain number of electron enclosed in a given volume is the aim of this work. The formulas to calculate them have been already developed and employed in atoms.[4] Now, the procedure will be employed in a selected group of molecules where we divided the space in regions as it is done in the topologic analysis of the density, AIM,[2] or of the ELF.[3] In the next section the main definitions of probabilities and the way to calculate them will be presented. Then, the applications to molecules will be discussed.

Theory

The quantity to be studied is the probability of finding n electrons inside a volume Ω provided the other electrons are outside of this region ($\hat{\Omega}$). This probability is given by:

$$p(n) = \binom{N}{n} \int_{\Omega} d1d2 \ldots dn \int_{\hat{\Omega}} dn + 1 \ldots dN|\Psi|^2 \quad (1)$$

where $\int_{\Omega}$ means that the integration is performed only within Ω and Ψ is the N-electron wave function. The prefactor has to do with the indistinguishability of the electrons and an integration over all the spins is assumed. This compact formula is, of course, of no practical application and more computable equations have been elaborated (see, e.g., ref. 4). For single determinant wave functions, the only quantities needed to compute the probability $p(n)$ with n any number between 0 and N are the overlap integrals

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$w_{ij} = \int_\Omega \phi_i\phi_j$, where the ϕ_is are the orbitals present in the Slater determinant. The final formula is

$$p(n) = \frac{1}{n!}\sum_{i=0,\,N-n}\frac{(-1)^i}{i!}\int_\Omega \Gamma^{n+1} \tag{2}$$

where $\int_\Omega \Gamma^n$ is the integral over the region Ω of the reduced density matrix of order n, Γ^n. This integral is a linear combination of terms of the type $(TrS_\Omega^{m_1})(TrS_\Omega^{m_2})\ldots$ with S_Ω the matrix with elements ω_{ij} and the positive integers m_1, m_2, ... are any combination summing up to n (for more details, see ref. 4).

The volumes Ω considered in this work are the atomic basins defined in Atoms in Molecules (AIM) or those of the ELF that have been determined using the program TopMod.[5] Of course, the use of a single Slater determinant produces some errors. For the H_2 molecule at equilibrium distance, $p(1) \approx 0.6$, while for a spin-restricted single determinant it is equal to 1/2; at infinite separation the error becomes very important: $p(1)$ is equal to 1, while for a single determinant it stays at 1/2. Another example of the limitation due to the use of a single determinant may be cases when multiple resonance structures are expected ($A^{2+}B^{2-} \leftrightarrow A^{2-}B^{2+}$, as supposed, for example, for the PO bond[6]).

Another bias is due to the choice of the integration volumes. Recently, one of us[4] studied the division into volumes by maximizing the probability of having the desired number of electrons, i.e., in atoms, the radius of the sphere that maximizes the probability of having exactly the number of valence electrons. For the Zn atom, for example, the radius of the sphere obtained in this way is of 1.94 bohr while using the ELF as a separator yields a value of 1.81 bohr.[7]

It is also important to mention that often the averages are different from the maxima of distributions. A well-known example is the radial electron distribution of the H atom, having the maximum at the Bohr radius, but an average at 1.5 bohr. Another simple example is given by the hydrogen molecule, at infinite internuclear separation. By symmetry, the average number of electrons, on each of the atoms is equal to 1. In the ground state, this comes from $p(1) = 1$. In the ionic excited state, this comes from $p(0) = p(2) = 1/2$.

To understand better the calculated probabilities it is instructive to consider the case of completely independent particles. In this case, if one denotes by p_{indep} the probability to find one of the N electrons in the given volume, the probability of finding it outside this volume is $(1 - p_{\text{indep}})$. Hence, the probability to find n independent electrons in a given volume, $p_{\text{bin}}(n)$, is

$$p_{\text{bin}}(n) = \binom{N}{n} p_{\text{indep}}^n (1 - p_{\text{indep}})^{N-n} \tag{3}$$

The prefactor (N/n) comes from the indistinguishability of quantum particles. The last equation describes just a binomial distribution that yields an average number of electrons equal to Np_{indep}. Therefore, from the average number of electrons one can obtain the value of p_{indep} for a real interacting system. The difference between the calculated probability $p(n)$ and the one of the independent model system calculated from eq. (2)

$$\Delta p(n) = p(n) - p_{\text{bin}}(n) \tag{4}$$

is a good measure of the (Fermi and/or Coulomb) correlation among the electrons inside this volume. Take again the example of H_2. Because there are two electrons with antiparallel spin, they are independent at Hartree–Fock level. By symmetry the average number of electrons in the half-space containing one of the nuclei is 1, and $p_{\text{indep}} = 1/2$. This yields $p_{\text{bin}}(1) = 1/2$, $p_{\text{bin}}(0) = p_{\text{bin}}(2) = 1/4$. Correlation in the ground state increases $p(1)$ to $\approx$0.6, and decreases $p(0) \approx p(2)$ to $\approx$0.2. They yield Δp values of 0.1 and -0.05, respectively. At infinite internuclear separation this effect is increased, producing $\Delta p(1) = 1/2$ and $\Delta p(0) = \Delta p(2) = -1/4$.

Consider now two hydrogen molecules, which are infinitely far apart, and choose first Ω to be the half-space containing one of the molecules. Due to the independence of the two hydrogen molecules we have $p(2) = 1$ and $p(0) = p(1) = p(3) = p(4) = 0$. This yields a significantly large $\Delta p(2) = 1 - 6/16 = 5/8$.

Take now Ω so that it contains half of each of the molecules. Let $p_m(n)$ be the probabilities for finding n electrons in the half-space defined by a plane perpendicular to the H—H bond on one of the hydrogen molecules. In this case, the probabilities are related according to the following $p(0) = p_m(0)^2 = p(4) = p_m(2)^2$, $p(1) = 2p_m(0)p_m(1) = p(3) = 4p_m(1)p_m(2)$, and $p(2) = 2p_m(0)p_m(2) + p_m(1)^2$. If each of the molecules is treated at Hartree–Fock level, $p_m(0) = p_m(2) = 1/4$, $p_m(1) = 1/2$, and we have $p(0) = p(4) = 1/16$, $p(1) = p(3) = 4/16$, and $p(2) = 6/16$, which corresponds again to the binomial distribution. When we take the true $p_m(n)$ ($\approx$0.2, 0.6, .02 for $n = 0, 1, 2$, respectively) we obtain, for the latter Ω, $p(0) = p(4) = 0.04$, $p(1) = p(3) = 0.24$, and $p(2) = 0.44$, which gives only a relatively small change in the probabilities with respect to the binomial distribution (a small decrease in the probabilities, -0.02, -0.01, in the first cases, while for $\nu = 2$, a relatively small increase, $\approx$0.065).

This simple examples should not induce in error to believe that Hartree–Fock wave functions yield always independent particles. For more than two electrons in a given system, (or even for two electrons with parallel spin) the Pauli principles comes into play, and $\Delta p(n)$ is different from zero. For example, in atoms $\Delta p(n)$ is largest for the n corresponding to the separation into shells.[4]

Another useful distribution is a Gaussian distribution. Very often, a normalized Gaussian curve having the same average and variance as given by the problem considered gives a reasonably good fit to the values of $p(n)$. This seems to be in contradiction to the asymmetry of the $p(n)$ with respect to the average. Remember, however, that the fit is valid only for integer number between 0 and N, and the asymmetry shows up especially when n is close to 0 or N. The normalized Gaussian fit is not a general solution, as for very low fluctuations, the Gaussian functions tends to become a δ function, and thus larger than 1. This problem can be avoided by using a non-normalized Gaussian, the supplementary unknown being determined from $\Sigma_{n=1,N}\, p(n) = 1$, as it is done in refs. 8 and 9. Our experience shows that such a fit works nicely, and needs only the knowledge of the first- and second-order reduced density matrices. It is, however, important to note that in this case the Gaussian distribution does not apply to a fractionary number of electrons. Therefore, speaking about an average number of

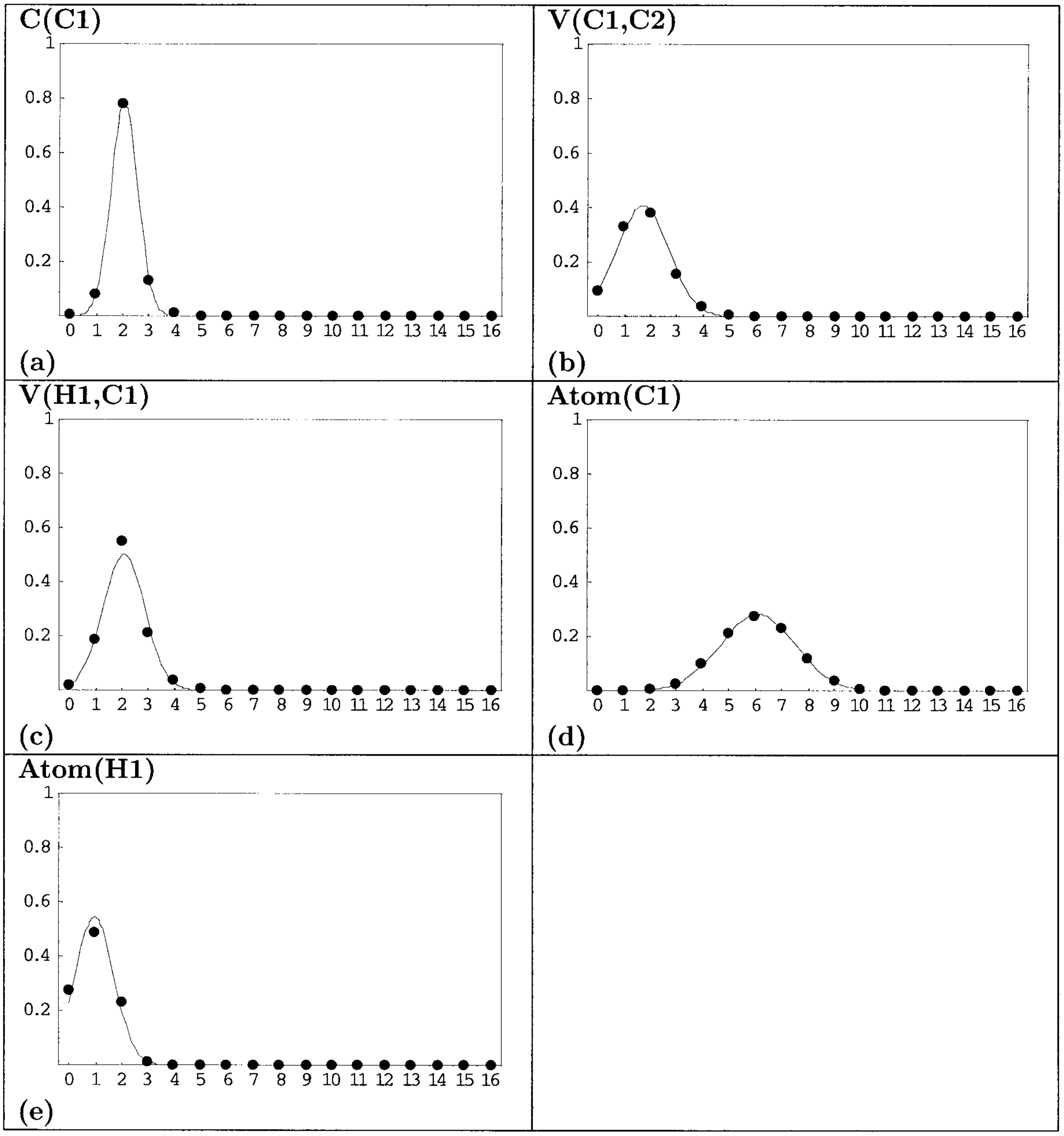

Figure 1. Probability distribution, $p(n)$, for C_2H_4. (a–c) ELF basins; (d–e) AIM basins. The solid line corresponds to the Gaussian fit.

N plus or minus some number obtained from the variance is not consistent with the present fit.

Computational Details

The electronic structure of most of the molecules studied on this work have been calculated at the level of theory presented in ref. 10. The basis sets are of the type 6-311++G** or 6-31G** and the method of calculation Hartree–Fock or Kohn–Sham with the B3LYP functionals. The molecules that do not belong to this group have been optimized at the B3LYP 6-311++G** level of calculation with a 6-311++G** basis set. The single Slater determinant produced by this method has been then used to calculate the probabilities. In principle, there is a formal problem in this choice. The Slater determinant produced by the Kohn–Sham equations is not an obvious approximation to the wave function. However, the practice of the last 10 years has demonstrated that the Kohn–Sham

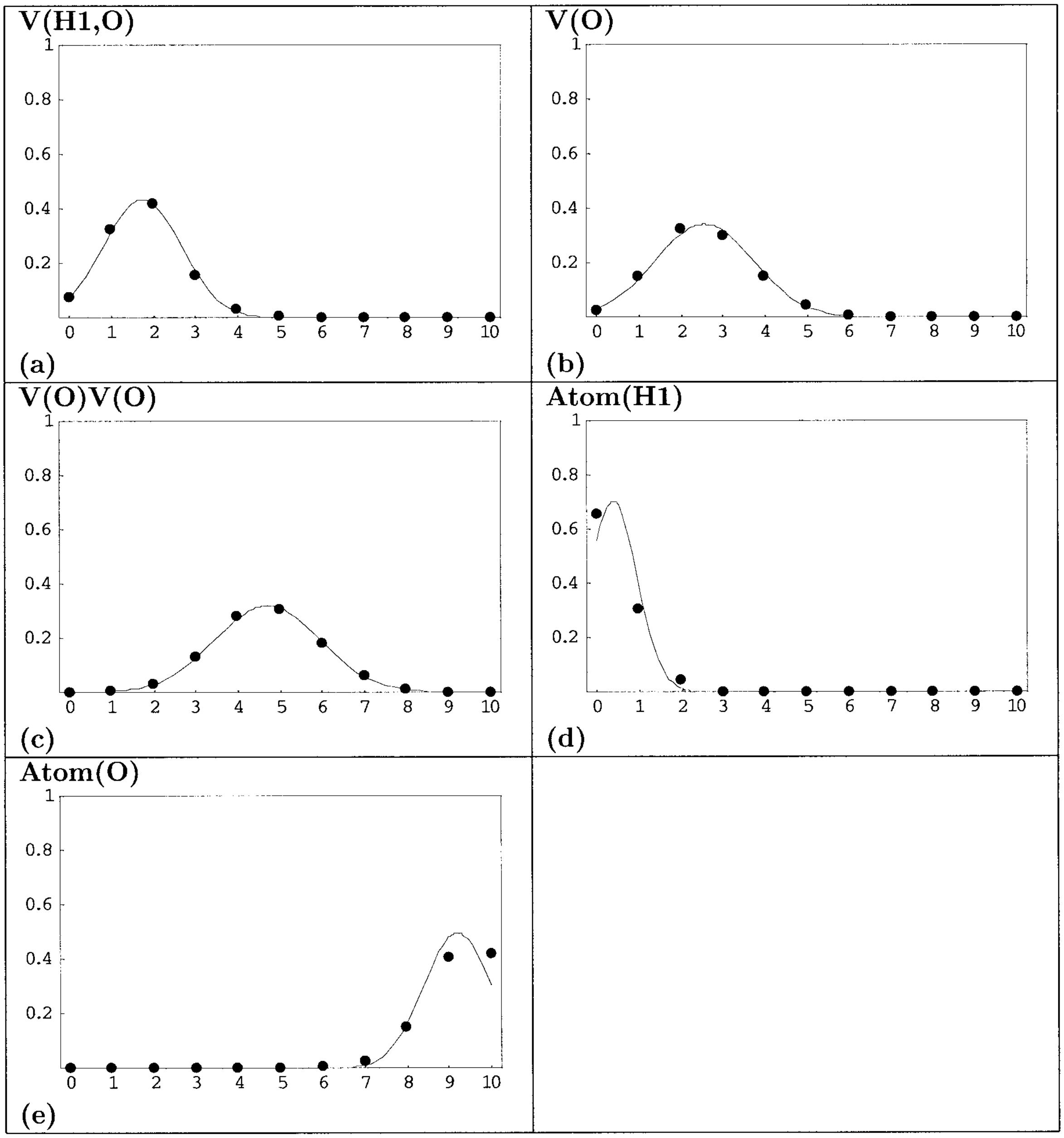

Figure 2. Probability distribution, $p(n)$, for H_2O. (a–c) ELF basins; (d–e) AIM basins. The solid line corresponds to the Gaussian fit.

orbitals are for most purposes similar to the Hartree–Fock ones.[11] Because the amount of data obtained is very high, additional tables and graphics not discussed below can be taken from the Web page www.lct.jussieu.fr/savin/publications.

Results and Discussion

First, general information of the calculated probabilities for a small selected group of molecules will be discussed. In Figures 1 to 5 the probability distribution for the AIM and ELF basins of the C_2H_4, H_2O, SF_3N, PF_5, and $P(CH_3)_5$ molecules are presented. Only the symmetry different basins are shown, and the continuous lines correspond to the Gaussian fit to the curves. The basins are named according to their chemical characteristics. A $C(X)$ basin corresponds to a core basin of the ELF associated to the atom X, and a $V(X, Y)$ basin corresponds to a bonding basin of the ELF associated to the X—Y bond, a $V(X)$ basin corresponds to a ELF basin associated to the lone pair of the atom X. The AIM basins are called according to the atom they belong to. In general, one can

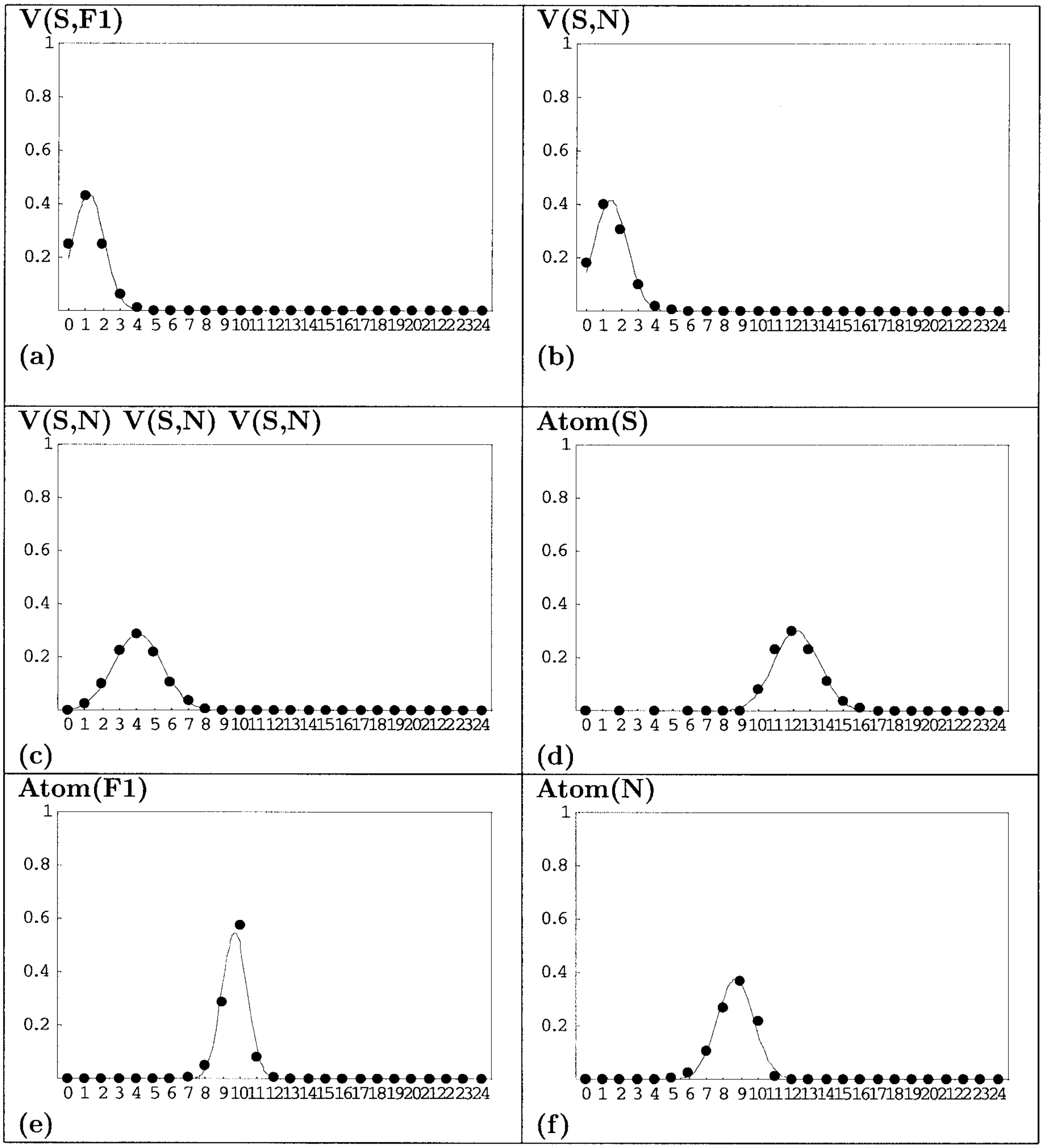

Figure 3. Probability distribution, $p(n)$, for SF_3N. (a–c) ELF basins; (d–f) AIM basins. The solid line corresponds to the Gaussian fit.

observe that the Gaussian fit works very well, and it is slightly better for the ELF basins. In the more polar molecules the probability distribution for the AIM basins is more asymmetrical and, therefore, has less resemblance to a Gaussian.

In Figure 1, the probabilities of finding n electrons, with n going from 0 to 16, for the ELF and AIM basins of the C_2H_4 molecule are presented. In the first panel, a, one can see the probabilities for the core basin of the carbon atom. The maximum is for $n = 2$ and the curve, which is slightly asymmetric, goes very fast to zero. In general, in this molecule the maximum for the ELF basins appears for $n = 2$. For the AIM basins the situation is different because here the basins represent the atom as a whole. The maximum in the carbon atom basin, panel d, occurs for $n = 6$ as expected. It is, however, interesting to note that the probability of finding as many as eight electrons which

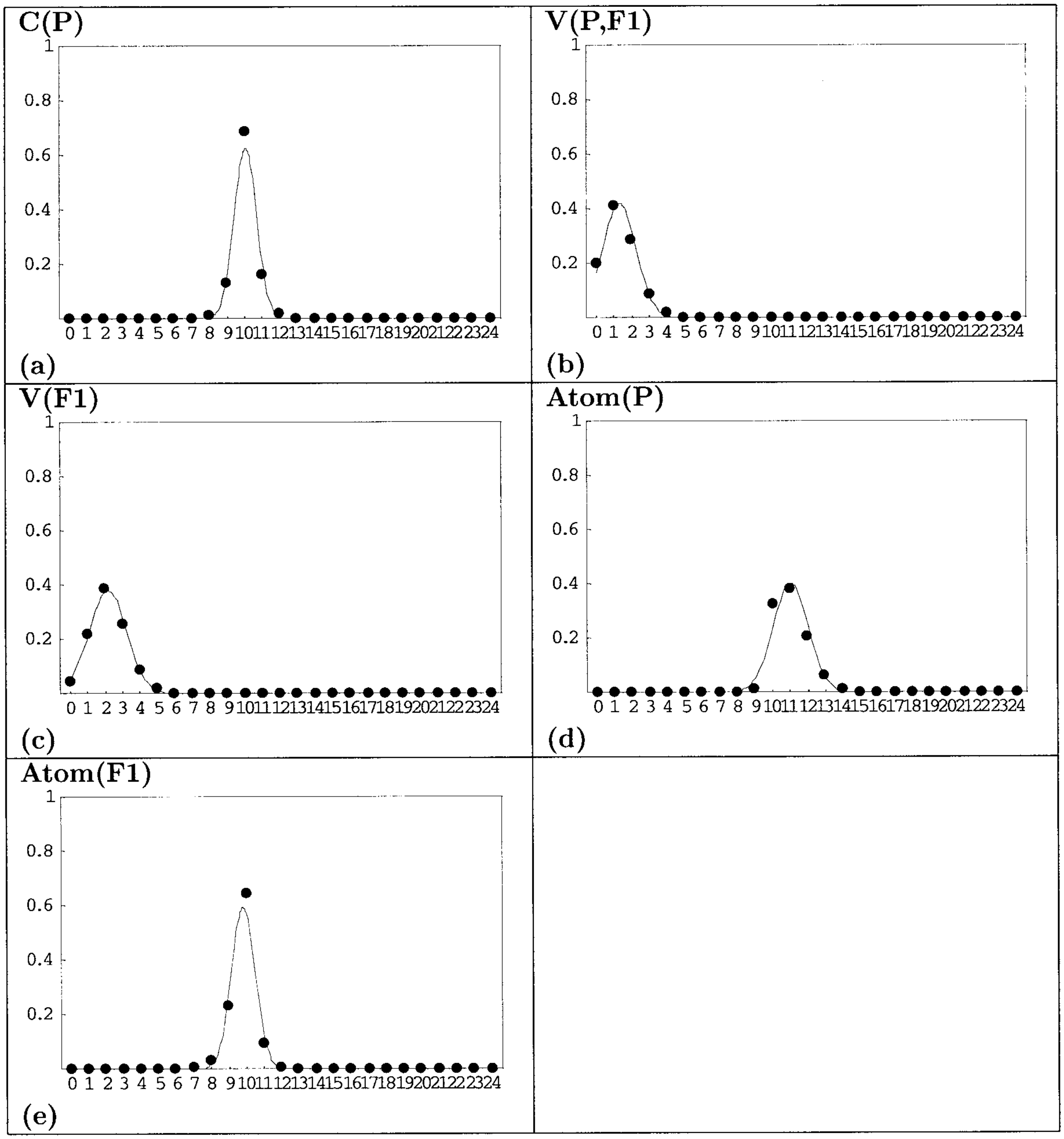

Figure 4. Probability distribution, $p(n)$, for PF_5. (a–c) ELF basins; (d–e) AIM basins. The solid line corresponds to the Gaussian fit.

is equivalent to have C^{-2} or as few as four electrons, C^{2+}, is not zero. However, it is important to remember that these numbers may be exaggerated by single determinant wave functions, which gives to much weight to the ionic structures.

In Figure 2, one can see the probability distribution for the most relevant basins of the H_2O molecule. In panel b it is one of the ELF basins associated to the lone pairs at the oxygen atom. There is another one that is identical by symmetry. The maximum in the probability is at $n = 2$. However, when the probabilities are calculated for the region of the space resulting from the merging of the two basins the maximum occurs at $n = 5$ as can be seen in panel c. This could be due to the polarity of the OH bond. This effect is also present in the AIM basins where the basin associated to the oxygen atom has a maximum in the probabilities at $n = 9$, O^-, and 10, O^{2-} (panel e). Note also in panel d that the maximum probability for the hydrogen atoms is to have zero electron, H^+.

In Figures 3 to 5, the probability distribution for some of the basins of the ELF and AIM of the molecules of SF_3N, PF_5 and

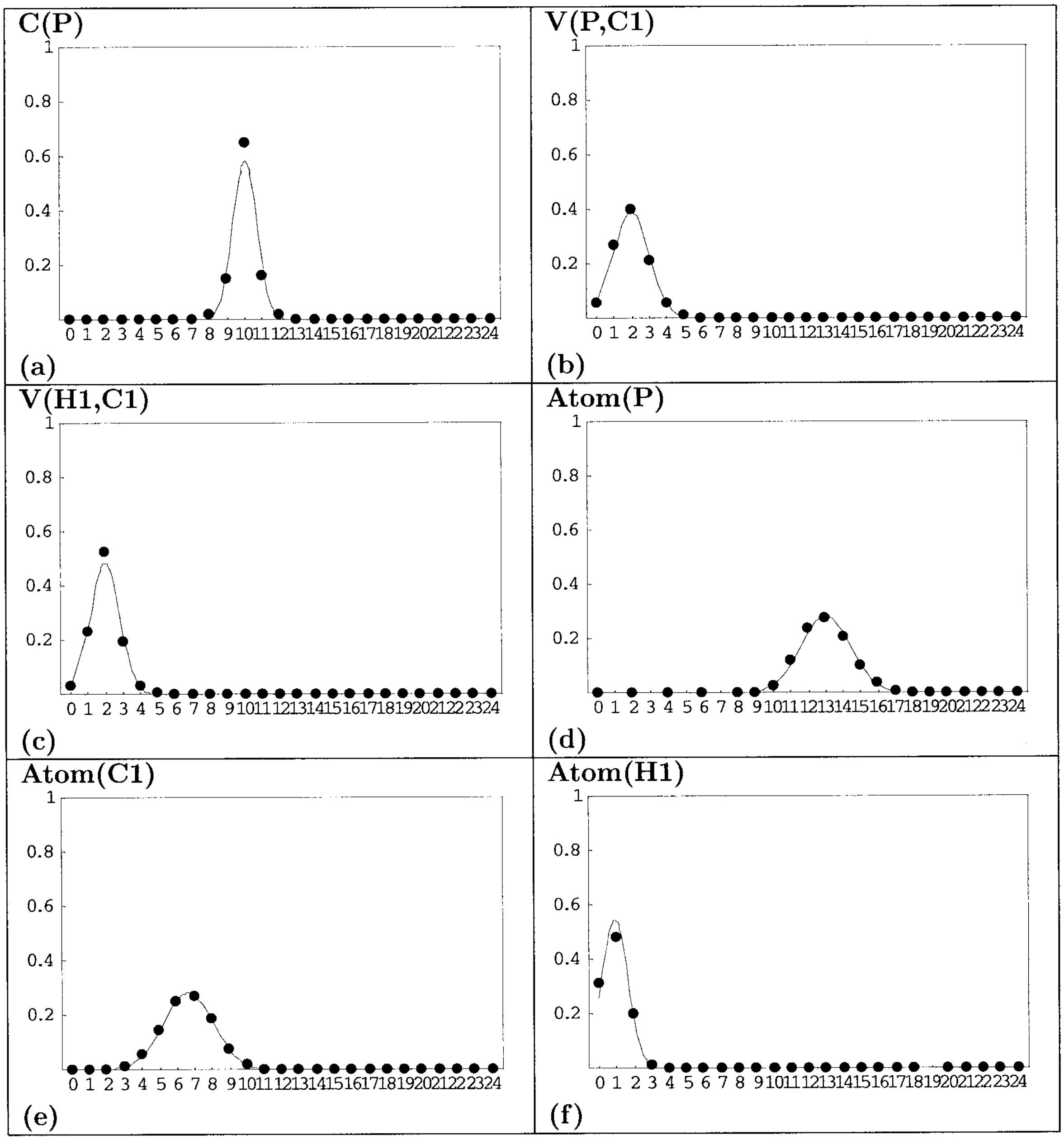

Figure 5. Probability distribution, $p(n)$, for $P(CH_3)_5$. (a–c) ELF basins; (d–f) AIM basins. The solid line corresponds to the Gaussian fit.

$P(CH_3)_5$ are presented. It is to see that the maximum in the basins associated to the SF, PF, and SN bonds occurs at $n = 1$ reflecting the high ionicity of the bonds, as defined by ELF. On the contrary, the maximum in the basin associated to the PC bond in the $P(CH_3)_5$ molecule occurs at $n = 2$. Notice that the merging of the basins associated to the SN bond in the SF_3N molecule, panel c in Figure 3, shows a maximum in the probability distribution at $n = 4$, and the probability of having six electrons, as in a triple bond, is as low as the probability of having two electrons. It is also interesting to compare the probability distributions in the AIM basins of the PF_5 and $P(CH_3)_5$ molecules (Figs. 4 and 5, respectively). In PF_5, the basin associated to the phosphorus atom (Fig. 4, panel d) presents a maximum at $n = 11$ with a high probability of finding 10 electrons, whereas in $P(CH_3)_5$, the maximum for the corresponding basin (Fig. 5, panel d) is at $n = 13$, with a high probability of having either 12 or 14 electrons. This is a consequence of the high polarity of the PF bond in comparison to the PC bond. This is also reflected in the probability distribution associated to

Table 1. Some Probabilities for the AIM Basins.

Basin	Molecule	$p(n = Z)$	$n_{\max}$	$p(n_{\max})$	n_Δ	n_Δ
Li	LiH	0.10	2	0.89	2	0.52
B	BH	0.29	4	0.62	2	0.30
C	CH_4	0.28	6	0.28	6	0.03
C	C_2H_4	0.27	6	0.27	6	007
C	C_2H_2	0.28	6	0.28	6	0.07
N	NH_3	0.21	8	0.33	8	0.02
O	H_2O	0.15	10	0.42	9	0.03
F	HF	0.24	10	0.74	9	0.02
P	PF_5	0.00	11	0.38	11	0.22
P	PFO_2	0.00	11	0.34	11	0.18
P	PF_3O	0.00	11	0.37	11	0.21
P	PH_3CH_2	0.07	13	0.28	13	0.11
P	$P(CH_3)_5$	0.10	13	0.28	13	0.11
S	SF_6	0.00	11	0.30	11	0.14
S	SF_4O	0.00	12	0.30	11	0.14
S	SF_3N	0.00	12	0.30	12	0.14

$p(n = Z)$ is the probability of finding Z electrons in the corresponding basin. $n_{\max}$ is the number of electron for which the probability is maximum. $p(n_{\max})$ is the probability of finding this number of electron. n_Δ is the number of electron for which the difference of probabilities defined in eq. (4) is a maximum. n_Δ is the value of this difference of probabilities.

the F or C atoms in the respective molecules. The fluorine atom basin in PF_5 (Fig. 4, panel e) shows a maximum at $n = 10$, whereas the carbon atom basin in $P(CH_3)_5$ (Fig. 5, panel e) shows a maximum at $n = 7$ with a high probability of finding six electrons.

In Table 1, for a series of molecules various probabilities associated to the AIM basins have been shown. They are, from left to right, the probability of finding Z electrons in the corresponding atomic basin, $p(n = Z)$, the number of electrons for which the probability is a maximum, $n_{\max}$, the probability of finding this number of electrons, $p(n_{\max})$, the number of electron for which the difference of probabilities defined in eq. (4) is maximum, n_Δ, and finally, the value of this difference of probabilities, $\Delta p(n_\Delta)$. The probability of finding Z electrons in the atomic basin is always very low. For instance, in molecules like CH_4, C_2H_4, or C_2H_2 the probability of finding six electron in the atomic carbon basin is as low as ≈ 0.3, despite having an average number of electrons in the basin of approximately 6. Looking at the hydrides of the elements of the second period it seems that the probability of finding Z electrons in the respective atomic basin is greater for the less polar bonds with the only exception of HF, which may be due to the high probability of having a fluorine atom with a charge of -1. A similar trend can be found for the maximum in the probability distribution which has a maximum for LiH and HF. It is also interesting to note that there is almost no difference between the basins associated to the carbon atom in CH_4, C_2H_4, or C_2H_2. For the basins associated to atoms of the third period the situation is different. The probability of finding Z electrons is almost always zero with the only exception of the basins associated to the phosphorus atom in the molecules of PH_3CH_2 and $P(CH_3)_5$, where the probability is low but different of zero. Furthermore, these two molecules are the ones with the greatest value of $n_{\max}$.

Table 2. Some Probabilities, for Having More Than Eight Electrons in ELF Basins Surrounding a Given Core, $p_{>8}$, and for Core ELF Basins.

Basin	Molecule	$p_{>8}$	$n_{\max}$	$p(n_{\max})$	n_Δ	$\Delta p(n_\Delta)$
Li	LiH	0.0	2	0.93	2	0.55
B	BH	0.00	2	0.85	2	0.52
C	CH_4	0.07	2	0.77	2	0.47
C	C_2H_4	0.18	2	0.78	2	0.49
C	C_2H_2	0.15	2	0.77	2	0.48
N	NH_3	0.09	2	0.75	2	0.45
O	H_2O	0.09	2	0.72	2	0.42
F	HF	0.12	2	0.70	2	0.40
P	PF_5	0.18	10	0.68	10	0.52
P	PFO_2	0.04	10	0.65	10	0.49
P	PF_3O	0.03	10	0.65	10	0.49
P	PH_3CH_2	0.89	10	0.65	10	0.49
P	$P(CH_3)_5$	0.76	10	0.65	10	0.52
S	SF_6	0.27	10	0.66	10	0.49
S	SF_4O	0.23	10	0.65	10	0.49
S	SF_3N	0.30	10	0.65	10	0.48

Because the ELF basins are of various kind (core, bonding, and lone pairs) the analysis of the data should be different. One can look, for instance, at the probability of having more than eight electrons around the central atom, which in Table 2 is called $p_{>8}$. The maximum of the probability distribution and of the probability difference of eq. (4) can be analyzed in a separate way for the core,

Table 3. Some Probabilities for the Bonding ELF Basins.

Basin	Molecule	$n_{\max}$	$p(n_{\max})$	n_Δ	$\Delta p(n_\Delta)$
LiH	LiH	2	0.91	2	0.54
BH	BH	2	0.73	2	0.40
CH	CH_4	2	0.54	2	0.23
CH	C_2H_4	2	0.55	2	0.26
CH	C_2H_2	2	0.51	2	0.23
CH	PH_3CH_2	2	0.52	2	0.23
NH	NH_3	2	0.47	2	0.17
OH	H_2O	2	0.42	2	0.13
FH	HF	1, 2	0.38, 0.37	2	0.09
PH	PH_3CH_2	2	0.58	2	0.30
CC	C_2H_4	2	0.38	2	0.10
C═C	C_2H_4	3, 4	0.32, 0.30	3, 4	0.08, 0.08
C≡C	C_2H_2	5, 6	0.33, 0.29	5, 6	0.11, 0.10
PC	PH_3CH_2	2	0.38	2	0.10
P═C	PH_3CH_2	4	0.32	4	0.11
PF	PF_5	1	0.41	1, 2	0.05, 0.05
PF	PFO_2	1	0.43	1	0.05
PF	PF_3O	1	0.43	1	0.05
SF	SF_6	1	0.42	1	0.05
SF	SF_4O	1	0.43	1	0.05
SF	SF_3N	1	0.43	1	0.06
SN	SF_3N	4	0.29	4	0.07
SO	SF_4O	1	0.43	1	0.05
S═O	SF_4O	2	0.34	2	0.06

Table 4. Some Probabilities for the Lone Pair ELF Basins.

Basin	Molecule	$n_{\max}$	$p(n_{\max})$	n_{Δ}	$\Delta p(n_{\Delta})$
B	BH	2	0.71	2	0.38
N	NH_3	2	0.42	2	0.12
N	SF_3N	4	0.33	4	0.11
O	H_2O	4, 5	0.31	4, 5	0.08, 0.07
F	HF	6	0.36	6	0.11
F	PF_5	6, 7	0.32, 0.33	6, 7	0.13, 0.16
F	SF_6	7	0.35	7	0.17
SF	SF_4O	1	0.43	1	0.05

bonding and lone pairs basins which is done in Tables 2 to 4, respectively. The analysis of the probabilities for the core basins is rather trivial. It yields a high probability of finding the expected number of electrons, i.e., two for the atoms of the second period and 10 for the atoms of the third period, with a high correlation. In Table 2, the interesting data come from the defined $p_{>8}$, the probability of having more than eight electrons around the central atom, which is very low for almost all the central atoms with the clear exception of the phosphorus atom in the molecules PH_3CH_2 and $P(CH_3)_5$. Hence, they are the only molecules that can be classified as hypervalent according to this analysis. In Table 3 some probabilities associated to the bonding basins are depicted. In some cases, the differences are not numerically significant and two possibilities are shown (for HF, C_2H_4, and C_2H_2). The analysis of the data shows that the maxima in the probability distribution occurs at the number of electrons equal to 2 for the covalent bonds and 1 for the highly ionic bonds of the elements of the third period with fluorine or oxygen. It is also interesting to note the difference between basins corresponding to simple bond and the ones corresponding to a double bond. The former have clearly the maxima for $n = 2$, whereas the later for $n = 4$. Note that the SN bond in SF_3N, which according to the Lewis structure is a triple bond, presents a maximum for $n = 4$. In Table 4 the probabilities associated to the lone pairs basins for some selected group of molecules are presented. One can note that the nitrogen atom in the molecule of SF_3N presents a maximum in the probability distribution for $n = 4$, which is in perfect agreement with the maxima in $n = 4$ for the bond basin reinforcing the view of only a double bond between sulphur and nitrogen atoms.

Concluding, in this work the probability distributions of finding a certain number of electron enclosed in a given volume have been calculated and analyzed. Probabilities and averages are the quantities one can calculate according to the quantum mechanics. In this sense, this work complements the usual information given by the calculation of the average number of electrons in a region of the space. It is also clearly shown that average numbers do not mean that the situation has the highest probability, for example, $n = Z$ for atomic basins in CH_4. The analysis of bonding situation can be more nuanced now. High weights of ionic structures, analysis of hypervalency, mixed situations, and other bonding characteristics can be on this way analyzed. The specific calculations show in this work have, however, limitations. The choice of the basins has been arbitrary. A possible improvement could be done defining the basins as the ones that maximize $p(n)$. Work in this direction is in progress.[12] Another limitation comes from the used wave function. A wave function coming from a Quantum Monte Carlo calculation permits avoiding limitations of the Hartree–Fock one.[13] Furthermore, obtaining the $p(n)$ in such a context is very easy and fast.

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