An Introduction to the Electron Localization Function, ELF

P. Fuentealba [a], D. Guerra [b] and A. Savin [c]
[a] Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653,
Santiago, Chile.
[b] Universidad Técnica Federico Santa María, Casilla 110-V Valparaíso, Chile.
[c] Laboratoire de Chimie Theorique, CNRS et Universite Pierre et Marie Curie Paris VI
4, place Jussieu F-75252 Paris Cedex 5, France

> "Of course, perhaps Lewis put it the right way..."
> Agatha Christie, "The Hollow"

The role of Quantum Theory in Chemistry has almost one hundred years, and the advances have been important. Nowadays, it is possible to do quantitative predictions with chemical accuracy for middle size molecules and some type of calculations, especially density functional based methodologies, are routinely done in many chemical labs. The other very important aspect on the influence of quantum theory in chemistry is the one of understanding. There are many chemical concepts which can be understand only through the laws of quantum mechanics. This chapter is about understanding and not about the other very important issue of computing with chemical accuracy.

One of the most important models to understand chemistry is the electron pair of Lewis [1]. He put forward the model where in an atom or molecule "...each pair of electrons has a tendency to be drawn together". This very important model, which is at the very beginning of any General Chemistry textbook, has however an important problem. It goes again the Coulomb law. Lewis noticed it and he was further to even affirm that perhaps "...Coulomb's law of inverse squares must fail at small distances". This remarkable fact is to our knowledge never discussed in the textbooks. At that time Lewis had no knowledge of the development of quantum mechanics, and already in the thirties he retracted of this statement [2]. Now, the explanation of why the electrons have a tendency to be drawn together even against the Coulomb‘s law, it is found in the Pauli exclusion principle and the influence of the kinetic energy. The Pauli exclusion principle is not only the reason of this tendency but also of the existence of the periodic table of elements. Hence, it is the Pauli exclusion principle who makes chemistry as we know it.

Let us start with the Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \tag{1}$$

Of course, the Coulomb interaction appears in the Hamiltonian operator, $\mathcal{H}$, and is often invoked for interpreting the chemical bond. However, the wavefunction, Ψ , must be antisymmetric, i.e., must satisfy the Pauli exclusion principle, and it is this only fact which explain the Lewis model of an electron pair. It is known that all the information it is in the square of the wavefunction, $|\Psi|^2$, but it is in general much too complicated to be analyzed as such because it depends on too many variables. However, in the last time there have been some attempts [3]. Lennard-Jones [4] proposed to look at a quantity which should keep the chemical significance and nevertheless reducing the dimensionality. This simpler quantity is the reduced second order density matrix

$$P_2(x_1, x_2) = \frac{N(N-1)}{2} \int dx_3 ... dx_N |\Psi(x_1, x_2, x_3, ... x_N)|^2 \tag{2}$$

which depends only on three spatial coordinates, $\vec{r}$, plus spin, σ, for each of the electrons of the pair (x stands for the couple $\vec{r}\sigma$). Hence, $P_2(\vec{r_1}\sigma_1, \vec{r_2}\sigma_2)$ times an infinitesimal volume element squared is interpreted as the probability to find one electron with spin σ_1 in a volume element around $\vec{r_1}$, and another electron with spin σ_2 in a volume element around $\vec{r_2}$. The prefactor comes from the fact that electrons are indistinguishable. Notice the analogy with the one–particle density $\rho(x)$,

$$\rho(x) = N \int dx_2 ... dx_N |\Psi(x_1, x_2, x_3, ... x_N)|^2 \tag{3}$$

which is related to the probability to find a particle with spin σ around $\vec{r}$.

It is evident that Lennard–Jones was following the track opened by Lewis, by concentrating on the pair of electrons. To get some insight into $P_2(x_1, x_2)$ it is natural to start with the simplest antisymmetric wave function, a Slater determinant constructed by real orbitals. In this case, one obtains

$$P_{2,det}(x_1, x_2) = \frac{1}{2}\left[\rho_{\sigma_1}(\vec{r_1})\rho_{\sigma_2}(\vec{r_2}) - \delta_{\sigma_1,\sigma_2}\gamma_{\sigma_1}(\vec{r_1}, \vec{r_2})^2\right] \tag{4}$$

where ρ_σ is the σ-spin component of the electron density:

$$\rho_\sigma(\vec{r}) = \gamma_\sigma(\vec{r}, \vec{r}) \tag{5}$$

and

$$\gamma_\sigma(\vec{r_1},\vec{r_2}) = \sum \phi_i(\vec{r},\sigma)\phi_i(\vec{r'},\sigma) \tag{6}$$

where the ϕ_i are the spin orbitals making the Slater determinant. To understand the features of $P_{2,det}$ it is useful to consider that the ϕ_i are localized. There is no loss of generality, as $P_{2,det}$ is invariant with respect to rotations among the orbitals. A further simplification makes it particularly easy to see how $P_{2,det}$ behaves. Imagine that the space can be divided into regions Ω_i , such that the localized orbitals ϕ_i satisfy the following relationship

$$\phi_i(\vec{r},\sigma) = \begin{cases} \sqrt{\rho_\sigma(\vec{r})} & \text{for } \vec{r} \in \Omega_i \\ 0 & \text{for } \vec{r} \notin \Omega_i \end{cases} \tag{7}$$

In this case

$$\gamma_\sigma(\vec{r},\vec{r'}) = \begin{cases} \sqrt{\rho_\sigma(\vec{r})\rho_\sigma(\vec{r'})} & \text{for } \vec{r},\vec{r'} \in \Omega_i \\ 0 & \text{otherwise} \end{cases} \tag{8}$$

Now, using Eq. (4) one can construct the reduced second order density matrix. For $\sigma_1 \neq \sigma_2$, $P_{2,det}$ is quite boring

$$P_{2,det}(\vec{r}_1\sigma_1,\vec{r}_2\sigma_2) = \frac{1}{2}\rho_{\sigma_1}(\vec{r}_1)\rho_{\sigma_2}(\vec{r}_2) \tag{9}$$

Hence, the probability of finding one electron with spin α around $\vec{r}_1$ and another with spin β around $\vec{r}_2$ is just the product of the probabilities of finding one particle in the given positions. The probabilities are independent which means the behavior of electrons are not correlated. However, for the case of two electrons with the same spin:

$$P_{2,det}(\vec{r}_1\sigma,\vec{r}_2\sigma) = \begin{cases} 0 & \text{for } \vec{r},\vec{r'} \in \Omega_i \\ \frac{1}{2}\rho_\sigma(\vec{r})\rho_\sigma(\vec{r}_2) & \text{otherwise} \end{cases} \tag{10}$$

the probability changes dramatically when one of $\vec{r}_1, \vec{r}_2$ share the same Ω or not. Imagine exploring space with a probe electron in $\vec{r}_1$. P_2 is zero for a whole region $\vec{r}_2 \in \Omega_i$, for all $\vec{r}_1 \in \Omega_i$. The moment $\vec{r}_1$ leaves this region, all probabilities change because a new region is defined. Thus, the electrons with spin α or β partition the space into regions Ω_i. For a closed shell system, the picture is even more simple, as localized orbitals are the same for both spins, the regions Ω_i will be the same for both spins. In such a case, each region is occupied by a pair of electrons, one with α–spin and the other with β–spin. Moreover, each electron with spin α or β "excludes" another electron with the same spin from that region. This the ultimate explanation for the Lewis electron pair model. There is not a new attractive force between a pair of electrons. It is just a repulsion between electrons of the same spin due to Pauli‘s exclusion principle which explains the electron pair model of Lewis.

Let us now consider a simple example: four non–interacting fermions in a one–dimensional box, $x \in [0, \pi]$. The wavefunction is a Slater determinant with two doubly occupied orbitals:

$$\phi_k(x) = \sqrt{\frac{2}{\pi}} sin(kx), k = 1, 2 \tag{11}$$

To analyze $|\Psi|^2$ it is sufficient to consider $|\Psi_\alpha(x_1, x_2)|^2$ and $|\Psi_\beta(x_1, x_2)|^2$, where the index indicates the spin. As there are only two particles of a given spin, moving in one dimension, it is possible to plot $|\Psi_\sigma|^2$, as it is shown in Fig. 1 [5].

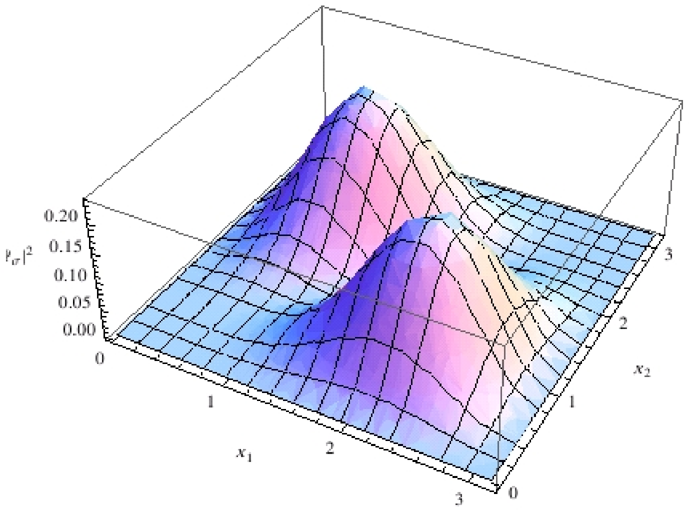


Figure 1: Plot of $|\Psi_\sigma|^2$, $\sigma = \alpha, \beta$ for four independent fermions in a box

One finds two maxima independent of the spin, one electron around $x \approx 0.955$ and the other one around $x \approx 2.186$. It is easier to understand the origin of the maxima by considering localized orbitals, $\psi = \frac{1}{\sqrt{2}}(\phi_1 \pm \phi_2)$. Both couples of orbitals are shown in Fig. 2 , and in Fig. 3 the one-particle density is shown.

Remember that the square of the wavefunction, or any of the reduced density matrices, are independent of a unitary transformation of the orbitals. Hence, any pair of orbitals is as good as the other. However, the chemical picture of molecular orbitals is easily understood for most of the chemists. In this case, it is easier looking at the localized orbitals. What the plot of $|\Psi_\sigma|^2$ tell us, is that the maxima are located close to the maximum of each orbital, and taking into account that each orbital is occupied by two electrons, one of

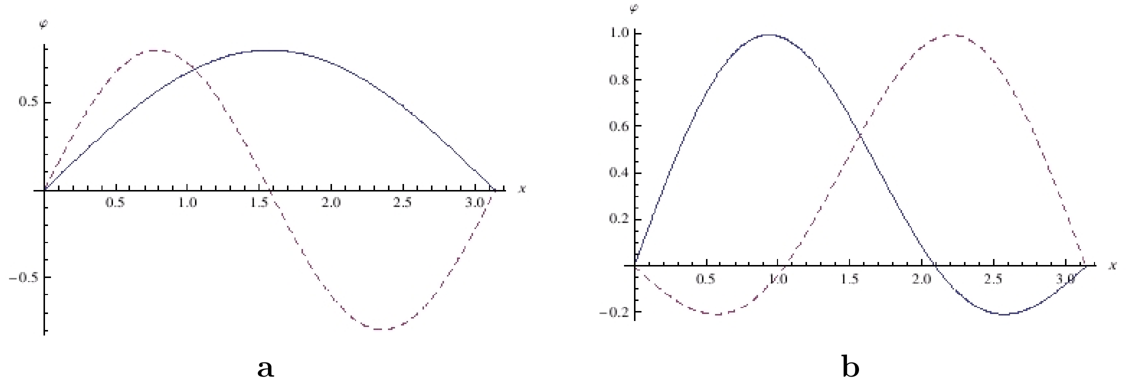


Figure 2: (**a**) Two lowest energy orbitals, ϕ_1, ϕ_2 for particles in a box and (**b**) two localized orbitals, for four independent fermions in a box.

each spin, the two maxima show us the regions where is most probable to find an electron pair in the sense of Lewis.

Let us now look at the one particle density, and compare it with the pair density $P_2(x_1\sigma, x_2\sigma')$.

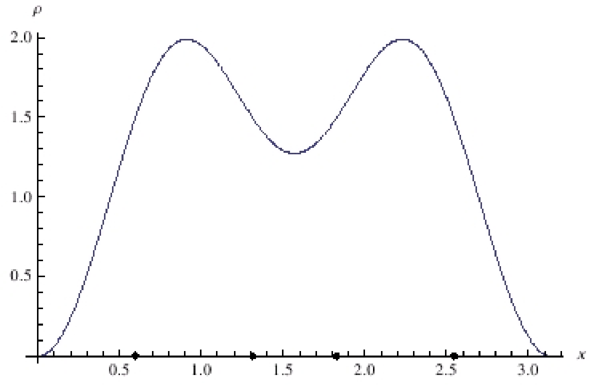


Figure 3: One-particle density for four no-interacting fermions in a one-dimensional box. The dots on the abscissa show different positions in which the density has the same value

We have to examine now the two posibilities, both electrons with the same spin or with different spin. In Fig. 4 we have the pair density for the case of different spin

It is clear that its structure correspond to the one of the one particle density because

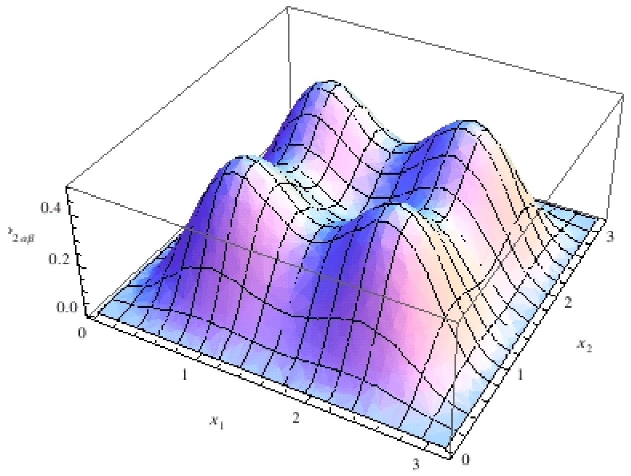


Figure 4: $\mathrm{P}_{2\mathrm{det}}(x_1, x_2)$ for fermions in a box, for $\sigma_1 = \alpha$ and $\sigma_2 = \beta$.

the probabilities are not correlated. However, for the case of the two electrons with the same spin the picture looks different (see Fig. 5).

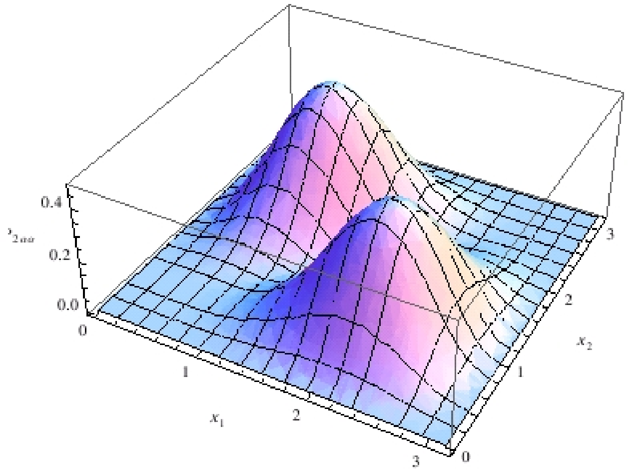


Figure 5: $\mathrm{P}_{2\mathrm{det}}(x_1, x_2)$ for fermions in a box, for $\sigma_1 = \sigma_2 = \alpha$.

Now, the probability of finding both electrons with the same spin around the same point, $x_1 = x_2$ has vanished, as the consequence of the Pauli principle. The box has been partitioned into its left and its right part. As long as one particle with one spin is in one part, it will impose the other electron of the same spin to be in the other half of the box. For example, we can consider the points chosen among those marked by dots on the abscissa on the Figure 3 showing the one-particle density. While for different spin P_2 will be the same for any pair of positions selected, this is not the case when both electrons have the same spin. When the spin is the same, and the electrons are on the points marked on the same half of the box, P_2 will be very small. However, if one point belongs to those on the left, the other to those of the right, P_2 is as large as for electrons with different spin.

Although the reduction of dimensionality by reducing $|\Psi|^2$ to P_2 is, in general, enormous, having to work in six dimensions is still difficult for human mind, and probably not needed for the analysis of the chemical bond: we see molecules in three dimensions. A way to further reduce dimensions has been noticed by Luken and Culberson [6] and by Becke and Edgecombe [7]. The idea is simple: as $P_2(\vec{r}_1\sigma, \vec{r}_2\sigma)$ is relatively insensitive as $\vec{r}_1$ moves within a given region Ω_i, but changes suddenly as it moves to another region Ω_j, one could concentrate on the change of P_2. A simple way to look at it is to consider a small sphere which moves together with the reference electron in r_1 [8]. If the radius of the sphere is R, the probability to find two electrons of spin σ in this small sphere is:

$$\int_{\text{small sphere}} P_2(\vec{r}_1\sigma, \vec{r}_2\sigma) d^3r_2 = C(\vec{r}_1) \int r_{12}^2 d^3r_{12} + ... \tag{12}$$

where we have used the expansion:

$$P_2(\vec{r}_1\sigma, \vec{r}_2\sigma) = C(\vec{r}_1) r_{12}^2 + ... \tag{13}$$

We see immediately that as long as the sphere stays in one Ω_i the probability of having two electrons with the same spin in it is very small. When the sphere overlaps with two different Ω_i, the probability increases. How large should the sphere be. It turns out that it is useful to choose the sphere in such a way that the probability of having two electrons with opposite spin is the same, independently of $\vec{r}_1$ [11]. In other words, using the expression of $P_{2,det}(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2)$ for $\vec{r}_1 = \vec{r}_2, \sigma_1 \neq \sigma_2$,

$$\left(\frac{4\pi R^3}{3}\right) \propto 1/\rho(\vec{r}_1) \tag{14}$$

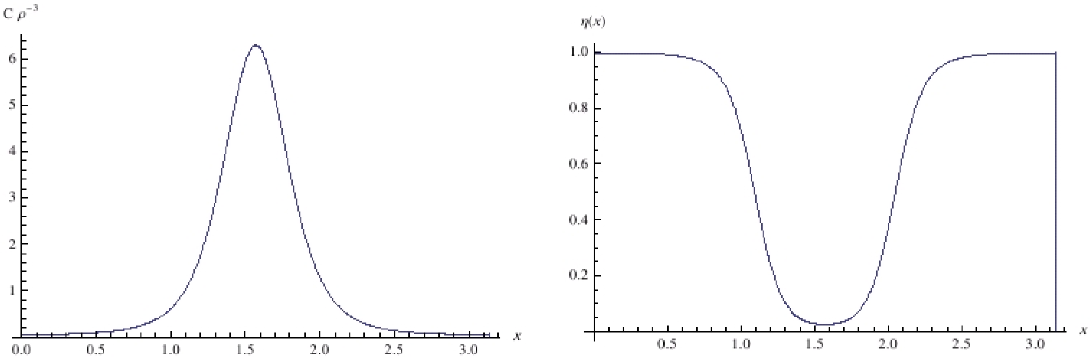
where we restricted the formula to the closed shell case. Thus, we get for the quantity of interest,

$$C(\vec{r})\rho(\vec{r})^{-5/3} \tag{15}$$

Kohout [9] used this function as an electron localization indicator (ELI). In the electron localization function (ELF), this function is scaled:

$$\eta(\vec{r}) = \left(1 + \kappa(C(\vec{r})\rho(\vec{r})^{-5/3})^2\right)^{-1} \tag{16}$$

where the constant κ comes from the proportionality relationship of above, but has now a well–defined value. On this way, the values of ELF ranges between zero and one. A large value of ELF, close to one, occurs when ELI is small, and it means a region where is probable to find an electron pair. A small value of ELF corresponds to a large value of ELI . Coming again to our example of four independent particles in a box, one can see in Fig. 10 both functions.



a **b**

Figure 6: (**a**) Cρ^{-3} for four particles in a one-dimensional box and (**b**) $\eta(x)$ for four particles in a one-dimensional box

It is clear that both functions are in some way the inverse of each other, but the interpretation is the same, the electron tend to localize at the borders of the box.

The final form of the ELF is

$$\eta(\vec{r}) = \left(1 + \left(\frac{D_P}{D_F}\right)\right)^{-1} \tag{17}$$

where

$$D_f = c_F \rho(\vec{r})^{5/3} \tag{18}$$

and

$$D_P = \frac{1}{2}\sum_i |\boldsymbol{\nabla}\phi_i|^2 - \frac{1}{8}\frac{|\boldsymbol{\nabla}\rho|^2}{\rho} \tag{19}$$

the first term on the right side represents the kinetic energy density of the noninteracting system and the second one is the von Weizsäcker kinetic energy density. This is the most important ingredient of the ELF, and the one which allows us a qualitative understanding of the relationship between the ELF and the exclusion principle of Pauli. The von

Weizsäcker kinetic energy is the exact kinetic energy functional for a system composed of non–interacting bosons, particles which do not follows the Pauli exclusion principle. It is also exact for the hydrogen atom or any other one particle system, the most localized system in a rigorous quantum mechanics sense. It is exact for the helium atom or any other two electron system in the Hartree–Fock approximation, the best examples of an electron pair. Hence for all those examples the term D_P will be exactly zero and the value of the ELF will be one. After helium atom the best examples of localized electron pair are surely the most inner electrons of any other molecular or atomic system, i.e., electrons with a configuration very close to $1s^2$, an the kinetic energy density of these pair of electron is surely very well approximated by the von Weizsäcker term. Hence in the regions very near to a nuclei the ELF will also have a value close to one. One can then hypothesize that the von Weizsäcker term will be a very good approximation in all regions where there is a localized electron pair. This is what we found in our example in Fig. 6b. Hence, the ELF appears to be a measure of the excess of kinetic energy density due to the exclusion principle [10]. The other terms of the function can be thought as a way to map a function which goes for minus infinity to plus infinity to a better behaved function which goes from zero to one.

The ELF was proposed by Becke and Edgecombe [7] in 1990 and very soon extensively applied to a variety of systems ranging from atoms to inorganic and organic molecules to solids [11] . In 1994 a topological analysis of the ELF was developed [13], which permit to do a more quantitative analysis of the three dimensional function. From that time until today the ELF has been extensively applied to a great amount of systems and has also been used to quantify other chemical concepts like strength of hydrogen bond [14] and aromaticity [15]. Beside the first review article [11, 12] there are other more recent review articles [16] where the reader can found a variety of different applications. In the final part of this article we will concentrate in one simple application of the ELF. Mainly we will analyze the ELF of the series of diatomic molecules of the type E_2 with $E = C$, Si, Ge, Sn and Pb on their triplet and singlet lowest states.

The atoms of the group 14 present a diverse chemistry. Whereas the first member of the series, carbon atom, is unique in the variety of bonding it forms, the other members change also the bonding nature because of the predominance of relativistic effects, mainly the spin–orbit coupling, in the last member of the series. For instance, the existence of a double bond in the family of molecules of the type $R_2C = CR_2$ is something obvious for any chemists student. However, for the rest of the series $R_2E = ER_2$ with $E =$ Si, Ge, Sn and Pb is by no way obvious. In fact, the most simple member of the series with $R = H$ does not exist. A nice application of the ELF to understand this type of bonds can be found in Ref. [18]. Within this context it appears interesting to look at the ELF of the homonuclear dimers E_2 in both, the singlet and triplet state. It is first necessary, however, a warning. The theoretical calculation of the electronic structure of the dimers of the group 14 is a very difficult task. It is one of this situation where the smallest molecules are the most difficult ones. Starting from C_2, which presents an important multideterminantal character of the wavefunction making hard to obtain quantitative results with any Kohn–Sham methodology, and finishing in Pb_2 where the spin orbit effects are very important making hard to obtain quantitative results using any one component scheme. Therefore, the present analysis it is only qualitative in an attempt to interpret the results obtained using a density constructed with Kohn Sham orbitals calculated using the Stuttgart pseudopotential [17] for all atoms. For the heavier atoms of Ge, Sn and Pb the small core pseudopotentials were used. The studied configurations are $\sigma_g^2\sigma_u^2\pi_u^1\pi_u^1\sigma_g^2$, $^3\Sigma_g$, for the triplets and $\sigma_g^2\sigma_u^2\pi_u^2\pi_u^2$, $^1\Sigma_g$, for the singlet in all molecules. Note that the configuration of the singlet state is unusual. The two σ orbitals do not contribute to the bonding because they are a bonding antibonding pair adding nothing to the bond order. Therefore, the state is stable only due to the existence of two bonding *pi* orbitals, and the molecules could be clasified as "only π bonding". This point has interesting consequence in the form of the ELF as we will see below.

In Table 1 one can see the calculated values of dissociation energy, HOMO-LUMO gap, triplet-singlet gap and bond length for the triplet and singlet states. In all molecules the triplet state is the lowest in energy in agreement with the experimental evidence. However, as stated above, the values are only a rough estimate of the experimental dissociation energies which are of 6.2 eV, 3.21 eV, 2.65 eV, 2.04 eV and 0.86 eV, for the dimers of C_2, Si_2, Ge_2, Sn_2 and Pb_2, respectively. The HOMO-LUMO gap are not so small in any case, but the presence of low lying states is known. It is also interesting to observe that the bond lengths of the singlet states are shorter than the ones of the triplet state which is the strongest bond. Hence those molecules do not obey the simple rule of: *the stronger the bond the shorter the bond length.* They do not follow the simple bond order of molecular orbital theory, because all of them present a bond order of two in the singlet as well as in the triplet state.

Let us look at the ELF of those molecules in Fig. 7. To look at a three dimensional function presents some ambiguities in the way the function is shown. We have chosen isosurfaces instead of maps of contours, and the value of the isosurface is arbitrary. However, for molecules of the second and third periods it is generally accepted that any value between 0.7 and 0.9 is good enough to represent the regions where is most probable to find localized electrons. For the heavier atoms where the d–electrons or f–electrons plays an important role, the ELF values are lower and the maxima are not greater than 0.7–0.8. Hence the isosurfaces to show the interesting regions are of around 0.3–0.5. This point, small values because of the presence of d–electrons, was first noticed by Kohout and Savin [19] and later on discussed by Burdett and McCornick [20] and Kohout et al [21]. The colors are also arbitrary. We have chosen red for the isosurfaces representing the core electrons, yellow for the bonding electron pair, blue for the lone pairs and green for the "not obvious" bonding electrons in the singlet states. For C_2 and Si_2 there are no

Table 1: Dissociation energy, HOMO-LUMO gap, triplet-single gap and bond length for the triplet and singlet states of the studied molecules.[a]

Dimer	multiplicity	D_e	Gap $_{\mathrm{H-L}}$	Gap $_{\mathrm{T-S}}$	Bond Length
C_2	triplet	5.33	2.55	0.62	1.372
	singlet	4.71	1.87		1.258
Si_2	triplet	2.96	1.91	1.10	2.304
	singlet	1.86	0.77		2.068
Ge_2	triplet	2.87	1.92	1.22	2.406
	singlet	1.65	0.60		2.176
Sn_2	triplet	2.40	1.73	1.22	2.781
	singlet	1.18	0.42		2.543
Pb_2	triplet	2.21	1.72	1.29	2.912
	singlet	0.93	0.33		2.678

[a] All energy values in eV and bond lengths in Amstrong

core basins because of the use of pseudopotential. Let start analyzing the triplet state. There is no evidence of a triple bond because of the existence of a lone pair behind the atoms (blue regions). The form of the isosurface for the bonding electrons is similar in all studied molecules, but it is getting smaller when one goes down the periodic table. For Pb_2 the isosurface of the basin representing the bond region is so small that it does not have the characteristics of the basins of the other molecules, and the form of the isosurface is more similar to the ones of the singlet that to the other molecules in a triplet state. The comparison from Ge_2 to Pb_2 shows clearly a change in the topology of the basin. It is interesting to note that for the lighter atoms the HOMO orbital is clearly the double occupied σ_g, whereas for Pb_2 it is the degenerate pair π_u, which are the HOMO in all the singlet states. This could explain the similarity in the form of the localisation domains. Remember that in the singlet state there is no σ bond. It is only a π bond with a nodal surface through the line connecting both atoms. The basins are cylindrical in shape and of other nature. They represent a pure π bond. One can speculate then that in the singlet state the bond length is shorter but weaker than in the triplet state because it does not have any σ bond.

References

[1] G. N. Lewis, J. Am. Chem. Soc, 38 (1916) 762

[2] G. N. Lewis, J. Chem. Phys. 1 (1933) 17

[3] E. Chamorro, P. Fuentealba and A. Savin, J. Comp. Chem. 24 (2003) 496

[4] J. E. Lennard–Jones, J. Chem. Phys. 20 (1952) 1024

[5] S. Wolfram, The Mathematica Book, Wolfram Media, Cambridge, 1996

[6] W.L. Luken and J.C. Culberson, Int. J. Quantum Chem. 16 (1982) 265

[7] A. D. Becke and K. E. Edgecombe, J. Chem. Phys. 92 (1990) 5397

[8] J. F. Dobson, J. Chem. Phys. 94 (1991) 4328

[9] M. Kohout, Int. J. Quantum Chem. 97 (2004) 651

[10] A. Savin, 0. Jepsen, J. Flad, 0. K. Andersen, H. Preuss, H. G. von Schnering, Angew. Chem. 104, 187 (1992); Angew Chem. Int. Ed. Engl. 31,187 (1992).

[11] A. Savin, R. Nesper, S. Wengert, Th. F. Faessler: Angew. Chem., 109, 1892 (1997), Angew. Chem Int Ed Engl 36, 1808 (1997)

[12] B. Silvi J. Phys. Chem. A107 (2003) 3081

[13] B. Silvi and A. Savin, Nature 371 (1994) 683

[14] F. Fuster and B.Silvi Theor. Chem. Acc. 104 (2000) 13

[15] J. C. Santos, W. Tiznado, R. Contreras and P. Fuentealba J. Chem. Phys. 120 (2004) 1670 ; J. C. Santos, J. Andres, A. Aizman and P. Fuentealba, J. Chem. Theory Comput. 1 (2005) 83

[16] P. Fuentealba, E. Chamorro and J. C. Santos in Theoretical Aspects of Chemical Reactivity Ed. by A. Toro, Elsevier 2007 ; J. Poater, M. Duran, M. Sola and B. Silvi Chem. Rev. 105 (2005) 3911

[17] B. Metz, H. Stoll, M. Dolg, J. Chem. Phys. 113, 2563 (2000)

[18] H. Grutzmacher and T. F. Fassler, Chem. Eur. J. 6 (2000) 2317

[19] M. Kohout and A. Savin, J. Comp. Chem. 18 (1997) 1431.

[20] J. Burdett and T. McCornick, J. Phys. Chem A102 (1998) 6366

[21] M. Kohout, F. Wagner and Y. Grin, Theor. Chem. Acc. 108 (2002) 150

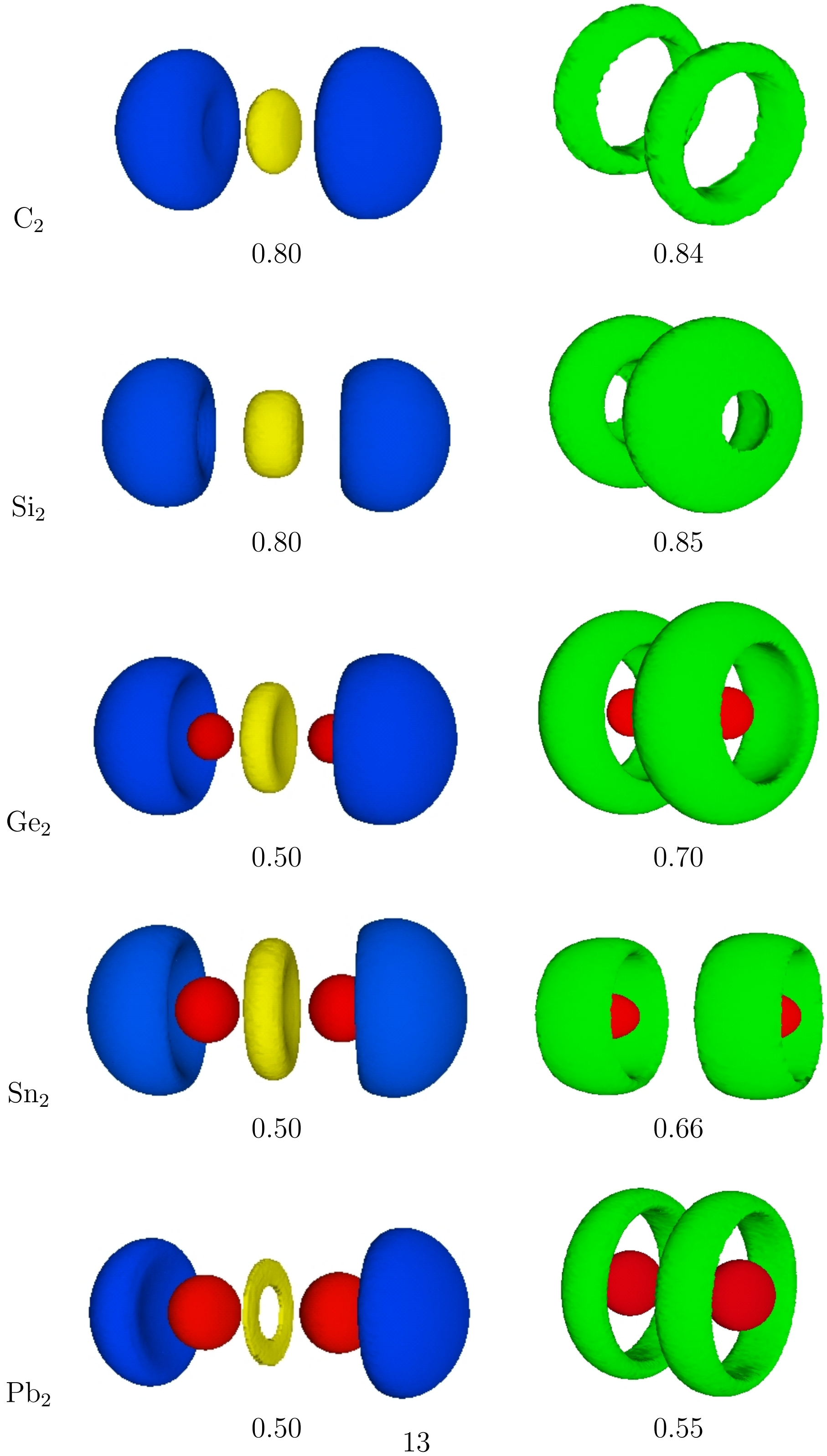


Figure 7: ELF isosurfaces for triplet (left) and singlet (right) of the different molecules. The values of the isosurfaces are indicated below each picture.