

On the significance of ELF basins

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Abstract. For perfectly localized orbitals, the basins of ELF are the domains in which the probability of finding a pair of electrons is maximal.

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1. ELF basins

The electron localization function (ELF) has been defined by Becke and Edgecombe¹ as a function of spatial coordinates which becomes large in the regions of space where electron pairs ‘localize’. For a closed-shell Slater determinant it is given by:

$$h(\mathbf{r}) = [1 + cy(\mathbf{r})^2]^{-1}, \quad (1)$$

where

$$y(\mathbf{r}) = [\mathbf{t}(\mathbf{r}) - (1/8)|\nabla\mathbf{r}(\mathbf{r})|^2/\mathbf{r}(\mathbf{r})]\mathbf{r}(\mathbf{r})^{-5/3}, \quad (2)$$

$$\mathbf{r}(\mathbf{r}) = \sum_{i=1, N/2} 2|\mathbf{j}_i(\mathbf{r})|^2, \quad (3)$$

is the electron density, N is the number of electrons in the system,

$$\mathbf{t}(\mathbf{r}) = \sum_{i=1, N/2} |\nabla\mathbf{j}_i(\mathbf{r})|^2, \quad (4)$$

is a local kinetic energy, and c is a constant which is set to make ELF equal to 1/2 for the uniform electron gas, but is irrelevant for the definitions of the basins of ELF, as these are determined by the directions of the gradients field of ELF, not their absolute values; the direction of ∇h is determined by that of ∇y uniquely:

$$\nabla h = -2cy(\mathbf{r})[1 + cy(\mathbf{r})^2]^{-2}\nabla y(\mathbf{r}). \quad (5)$$

ELF has been found to be very useful for the interpretation of the chemical bond, as it yields pictures for regions for electron pairs often close, sometimes to complement to chemical intuition (see, e.g., refs 2, 3). In a mathematically more rigorous way, such

regions, ELF basins,⁴ were defined following the spirit of Bader’s Atoms in Molecules (AIM). All points in space which lead to the a given maximum of ELF, by following the gradient of ELF, belong to the same basin. Basins provide a partition of space. *A priori*, as ELF is defined locally, the basins of ELF do not have a physical significance, even if several physical interpretations have been given to ELF (see, e.g., a recent discussion in ref 5). Due to the interest in applying ELF, it is worthwhile to try to understand the significance of ELF basins.

We will consider a different physical picture, namely that of regions where the probability to find a pair of electrons is maximal, and show that in the case of perfectly localized molecular orbital these regions are identical to the basins of ELF.

2. Probabilities

In contrast to the basin definition, Daudel and his coworkers (see, e.g., refs 6, 7) considered ‘loges’, domains in space which have a clear physical significance. Following this spirit, one can define regions of space where the probability of finding a number of electrons, n , is maximal. The probability of finding n electrons in the region Ω will be written $p(\mathbf{n}; \Omega)$, and a region where it is maximal, Ω_y . Numerical experience has shown that this criterion works well for finding regions corresponding to atomic shells,⁸ or bonds and lone pairs in molecules.^{9,10}

Recently, it was possible to derive formulas to determine $p(\mathbf{n}; \Omega)$ in an efficient way for wave functions described by one or a few Slater determinants.⁹ Of course, the probability can be determined also for more complicated wave functions, e.g., in quantum Monte Carlo,¹¹ by directly computing

$$p(\mathbf{n}; \Omega) = \binom{N}{\mathbf{n}} \int_{\Omega} d\mathbf{1} d\mathbf{2} \dots d\mathbf{n} \int_{\mathbb{R}^3 \setminus \Omega} d\mathbf{n} + 1 \dots dN |\Psi|^2 \quad (6)$$

where Ψ the wave function, and \int_{Ω} indicates that the integration is to be performed only over the domain Ω .

For a single Slater determinant the algorithm is the following. We first construct the matrix $S(\Omega)$, with elements,

$$S(\Omega)_{ij} = \int_{\Omega} \mathbf{j}_i \mathbf{j}_j, \quad (7)$$

where \mathbf{j}_i are the orbitals. Let the eigenvalues of $S(\Omega)$ be I_1, I_2, \dots . One gets for the probabilities:

$$\begin{aligned} p(0; \Omega) &= \prod_i (1 - I_i), \\ p(1; \Omega) &= \sum_j I_j \prod_{i(\neq j)} (1 - I_i), \\ p(2; \Omega) &= \sum_{j>k} I_j I_k \prod_{i(\neq j,k)} (1 - I_i). \end{aligned} \quad (8)$$

(For programming, a recursive expression can be used, cf. ref 9, but we will need here only the equations above.)

By the definition given for Ω_n , one can, in general, expect several solutions to the optimization problem. For example, for a pair of electrons, one expects an $\Omega_{n=2}$ for each chemical bond and for each lone pair in the system. Furthermore, while computing the $p(\mathbf{n}; \Omega)$ is not expensive, the algorithms we presently use, are still relatively time consuming. From this perspective, it would thus be useful to know whether one could use the ELF basins, which are cheaper, as a reasonable approximation to $\Omega_{n=2}$, or as a starting guess.

3. Perfectly localized orbitals

As it is well known, there are unitary transformations which yield molecular orbitals which are 'localized', in the sense that $|\mathbf{j}_i|^2$ is large only in a given region of space, L_i . In contrast to basins, or the Ω_n , these regions are not well-defined, except in the limiting case when orbitals are 'perfectly' localized, \mathbf{f}_i : \mathbf{f}_i are non-zero only for $\mathbf{r} \in L_i$.

Please note that as all L_k that are not localized in L_k are zero in L_k , the electron density in L_k is only given by the \mathbf{f}_k localized in it.

These perfectly localized orbitals never occur in a molecule, as this requires a sudden jump of L_i on the

border of L_i , which makes \mathbf{f}_i non derivable (infinite kinetic energy). To see it, one has to realize that the density will be nonzero in the molecule, also around the borders of L_i , and thus \mathbf{f}_i has to drop from a value which squared yields the density, inside L_i , to 0 outside L_i . Furthermore, in contrast to $p(\mathbf{n}; \Omega)$ which can be defined for any wave function, the picture of electron pairs resulting from localized orbitals, cannot. (The definition of ELF can be also generalized to any wave function, see, e.g., refs 3, 5.) The perfectly localized orbitals yield nevertheless a useful picture, to which we are accustomed.

4. Comparison of ELF basins with domains of maximal probability for perfectly localized orbitals

We will now consider a closed shell Slater determinant constructed from perfectly localized orbitals. In this case,

$$S_{ij}(L_k) = \mathbf{d}_{ij} \mathbf{d}_{jk}. \quad (9)$$

Thus, the matrix $S(L_k)$ is diagonal, having only two of its diagonal elements (for the two spin-orbitals localized in L_k) equal to 1, while all the others are 0. From (8),

$$p(\mathbf{n}; L_k) = \begin{cases} 1, & \mathbf{n} = 2, \\ 0, & \mathbf{n} \neq 2, \end{cases} \quad (10)$$

which is the best one can achieve for a probability. Thus, L_k is one of the $\Omega_{n=2}$. In a next step, one can consider a deformation of L_k , e.g., by choosing Ω such that it contains most of L_k , but not all of it. In this case, (9) is not valid any more, and the I_i will not all be equal to 0 or 1. (For example, one can consider $L_1 + \mathbf{d}\Omega$, which changes S_{11} and S_{33} to $S_{11}(\Omega) = 1 - \mathbf{d}_1$, $S_{33}(\Omega) = 0 + \mathbf{d}_3$, which yields $I_1 = 1 - \mathbf{d}_1$ and $I_3 = \mathbf{d}_3$.) According to (8), $p(2; \Omega)$ must now decrease.

Similarly, one can show that the ELF basin corresponds to L_k . To obtain this result, consider first \mathbf{r} inside L_k . As both spin-orbitals localized in L_k have the same spatial part, the density is simply given by $\mathbf{r}(\mathbf{r}) = 2|\mathbf{f}_k|^2$. Introducing it into (1), it yields $\mathbf{h} = 1$ inside L_k . At the border $\nabla \mathbf{f}_k$ becomes infinite, and thus $\mathbf{h} = 0$. One can imagine a slight smoothing, in order to obtain the basin which is the region of 'large' \mathbf{h} , L_k .

Finally, one can consider, as Bader and Stephens,¹² and more recently Ponc and Chavez,¹³ or Ayers¹⁴ the domains which minimize the fluctuation, or variance,

$$s^2(\Omega) = \sum_{\mathbf{n}} \mathbf{n}^2 p(\mathbf{n}; \Omega) - [\sum_{\mathbf{n}} \mathbf{n} p(\mathbf{n}; \Omega)]^2, \quad (11)$$

or related quantities, such as $s^2(\Omega)/\sum_{\mathbf{n}} \mathbf{n} p(\mathbf{n}; \Omega)$.

From the values obtained for $p(\mathbf{n}; L_k)$ one sees that choosing $\Omega = L_k$ also minimizes s^2 or $s^2(\Omega)/\sum_{\mathbf{n}} \mathbf{n} p(\mathbf{n}; \Omega)$.

5. Conclusion

Although ELF is locally defined, and the probability to find two electrons in a region of space Ω is not, it was shown that for perfectly localized orbitals, the domains where the probability to find two electrons is maximal corresponds to the basin of ELF. This regions are also those of minimal electron fluctuation.

One can now ask what happens in a realistic case. In some trivial cases, like He_2 , symmetry will also impose the same regions for $\Omega_{n=2}$ as for the basins of ELF. Numerical calculations (cf. refs 8, 10, 13) show that in many situations the basins of ELF are close to the regions of maximal probability.

There are, however, cases, where one may expect a different result, e.g., when localized orbitals cannot be uniquely defined for a given criterion, like in the Ne atom: localized orbitals or $\Omega_{n=2}$ will yield domains dividing the space into a core region, and four other valence region reminding of sp^5 orbitals, while ELF is symmetry adapted and gives only a spherical shell. Notice, however, that $\Omega_{n=8}$ is also an important $p(\mathbf{n}; \Omega)$ (cf. ref 8) and that $\Omega_{n=8}$ resembles to the ELF basin. Another example is that of the uniform electron gas.¹⁵ The probability of finding a pair of electrons in a sphere will be maximal for a finite radius, while ELF, being uniformly 1/2 in the

whole space does not define a basin with a finite, non-zero, volume. (Notice that minimizing $s^2(\Omega)/\sum_{\mathbf{n}} \mathbf{n} p(\mathbf{n}; \Omega)$ has a unique solution, the whole space.)

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