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The electron localization function (ELF) and its relatives: interpretations and difficulties

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Abstract

ELF is a function of the 3D-coordinates which is large in the regions where orbitals localize. It is closely related to LOL and the Fermi hole mobility function. While it has been used with considerable success for analyzing the chemical bond in molecules and crystals, it seems to have some intrinsic limits, which are discussed.

Keywords: Electron localization function; Localized orbital locator; Electrons

1. Definition of ELF

Since Becke and Edgecombe have introduced the electron localization function (ELF) [1], several applications have demonstrated its usefulness (cf., e.g. [2,3]). It is a function of the spatial coordinates, (x, y, z). For an independent-particle model, ELF can be computed from the orbitals, as its definition is:

$$\eta(\mathbf{r}) = \frac{1}{1+(D/D_\mathrm{h})^2},$$

$$D = \frac{1}{2}\sum_{i=1}^{N} |\nabla\psi_i|^2 - \frac{1}{8}\frac{|\nabla\rho|^2}{\rho}, \tag{1}$$

$$D_\mathrm{h} = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3}, \quad \rho = \sum_{i=1}^{N}|\psi_i|^2,$$

where the sum is over all singly occupied (spin-) orbitals $\psi_i(\mathbf{r})$. It turns out that, in general, ELF shows only little dependence on the method used, as long as the orbitals properly reflect the Pauli principle (cf., e.g. Fig. 5 in Ref. [4]). Even a simple method, such as EHT can yield reasonable ELF plots (see, e.g. Ref. [5]), while it is not clear how to use ELF in a zero differential overlap method like MNDO.

It will be shown below how the definition of ELF can be obtained from localized orbitals. Usually localized orbitals are obtained from canonical ones by a unitary transformation. Let us try to find a quantity, which is able to detect the regions where orbitals localize, without requiring the knowledge of the localized orbitals. In other words, we seek for a function, which is invariant to unitary transformations, so that it can be computed from the set of orbitals, no matter whether they are canonical or obtained by a localization procedure. It is not that we try to avoid the unitary transformation of orbitals: in general, it is not a computationally demanding task. The main reason is the fact that often the symmetry of system is not consistent with the number of localized orbitals. For example, in $B_6H_6^{2-}$ there are 14 cage electrons, so that 7 localized orbitals would be doubly occupied. It is impossible, however, to symmetrically distribute 7 localized orbitals over the octahedral cage. There will be (sometimes infinitely) many possibilities to localize orbitals in such cases (see, e.g. Ref. [7]): Numerics decide which localization is chosen. The price to pay for avoiding this problem is that an average picture is obtained. For example, for the Ne atom, instead of obtaining 4 valence ‘sp^3-hybrids’, arbitrarily oriented in space, one obtains a valence ‘shell’. A further detail to notice is that localized orbitals can be determined by infinitely many unitary transformations, so that we have some freedom in using the term ‘localization’).

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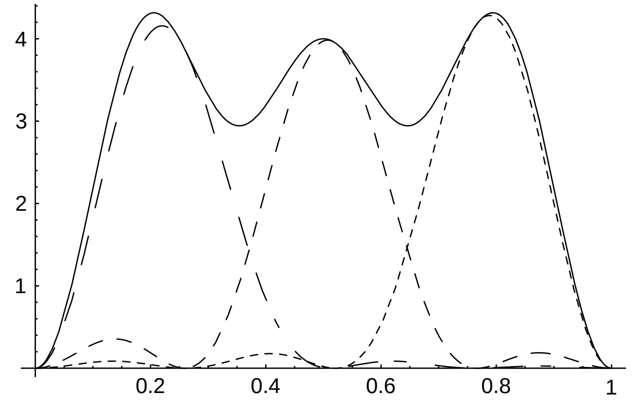

Fig. 1. The localized orbitals (squared), with dashed curves, and their sum, the density (full curve), as a function of the position.

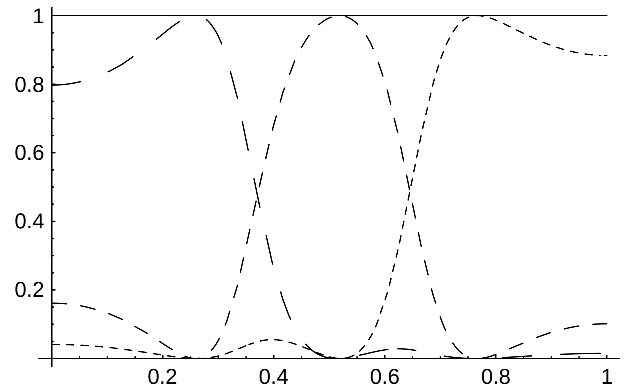

Fig. 2. The ratio between the localized orbitals and the square root of the density, squared (dashed curves), and their sum, equal to 1, full line, as a function of the position.

Let the localized orbitals be ϕ_i. In the region where ϕ_i is localized, $|\phi_i|^2$ is close to the density ρ (see Fig. 1[1]). This effect can be enhanced by showing $|\phi_i|^2/\rho = |\phi_i/\sqrt{\rho}|^2$ which is close to 1 in the localization region, and close to 0 outside it (see Fig. 2). Of course, ρ is invariant to orbital transformations, as is the sum over all $|\phi_i/\sqrt{\rho}|^2$.[2] As $\sum|\phi_i/\sqrt{\rho}|^2$ is always equal to 1, it does not seem to be useful, too. We can, however, try the trick applied by Bader and co-workers to the density [6], to extract more information: we will take derivatives. $|\nabla(\phi_i/\sqrt{\rho})|^2$ is a function which has significant values only on the border of the region where ϕ_i is localized, as $\phi_i/\sqrt{\rho}$ changes only little both inside and outside the domain where ϕ_i is localized, cf. Fig. 2. Let us define now $w = \sum|\nabla(\phi_i/\sqrt{\rho})|^2$. This quantity is positive, is large in the regions between those where orbitals localize: it describes 'walls' between which the orbitals localize, the electron pairs being confined to the 'wells' (cf. Fig. 3). Please notice that w is a function of the position, as are the ϕ_i, and is invariant to unitary transformations, due to the appearance of the sum. As the first-order density matrix is given by $\gamma(\mathbf{r},\mathbf{r}') = \sum\phi_i(\mathbf{r})\phi_i^*(\mathbf{r}')$, w can be also be re-written as

$$w(\mathbf{r}) = \nabla_{\mathbf{r}}\nabla_{\mathbf{r}'}\gamma(\mathbf{r},\mathbf{r}'/\rho(\mathbf{r})|_{\mathbf{r}'=\mathbf{r}}$$

explicitly showing the invariance.

We now have to come back to the case where the localization is not unique. In such a case w will show an 'average' effect. For example, in the uniform electron gas, the translational invariance produces an average value for w. This depends on the density of the gas which in three dimensions is given by:[3] $w \to w_{\mathrm{hom}}(\rho) = (3/5)(3\pi^2)^{2/3}\rho^{2/3}$. Taking into account the density variations within electronic systems, it seems that we might get a better measure for localization by using w_{hom} as a standard, e.g. by using w/w_{hom} (cf. Fig. 4).

ELF is obtained from w/w_{hom} via a transformation which has the maxima where w/w_{hom} has the minima:

$$\eta = \frac{1}{1 + \left(\frac{w(\mathbf{r})}{w_{\mathrm{hom}}(\rho(\mathbf{r}))}\right)^2}$$

Thus, ELF is small in the boundary regions of the localized orbitals, and is large (close to 1) within the regions of localization, cf. Fig. 5. For the uniform electron gas of any density it is equal to 1/2, it is invariant to unitary transformations, and is symmetry-adapted (via $\gamma(\mathbf{r},\mathbf{r}')$ and $\rho(\mathbf{r}) = \gamma(\mathbf{r},\mathbf{r})$).

2. Variations on the same subject

Many other interpretations of ELF are possible. One of them is to recognize that $1/2\rho w$ is the excess of the local, positive definite kinetic energy, due to the Pauli principle (and, of course, $1/2\rho w_{\mathrm{hom}}$ that of the uniform gas) [13]. As in independent-particle models the higher-order reduced density matrices can be described using γ, it is possible to give also further interpretations based on higher-order density matrices, as the original one given by Becke and Edgecombe [1] and others [3,14,15]. While all these interpretations are equivalent in independent-particle systems, this is not the case for the physical, interacting, system. There is not yet enough experience to distinguish between the different interpretations when using

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[1] All figures are schematic. They were drown for six non-interacting particles in a one-dimensional box, by taking into account in all definitions that only one dimension is present.

[2] While in Fig. 1, where the localized orbitals are produced for non-interacting particles in a box, the electron density shows minima which might be used to detect the regions where the orbitals are localized, this is not the case in molecular systems, where as a rule, the electron density shows maxima on the nuclei alone (cf. [6]), not permitting the separation we are following here.

[3] In one dimension, as used in the figures, it is given by: $\pi^2/3\rho^2$.

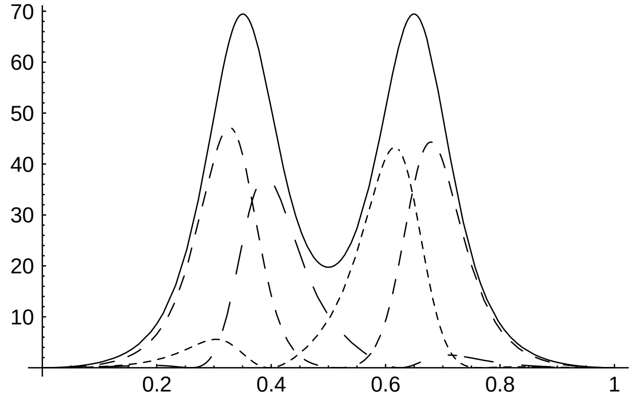

Fig. 3. The derivatives of the ratio between the localized orbitals and the square root of the density, squared (dashed curves), and their sum, *w*, full curve, which yields walls between the regions where orbitals localize, as a function of the position.

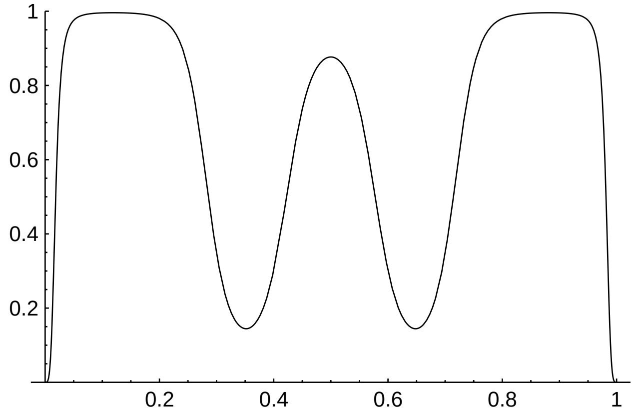

Fig. 5. The electron localization function, as a function of the postion, showing the regions where the orbitals localize by values close to 1.

the interacting system. Two ways were mainly considered up to now: The first one is to use the definition based on the difference between the local kinetic energy. This definition, making no use of the second-order density matrix is easy to use. One might prefer, however, the second one, which is to keep to non-interacting systems, as the Kohn-Sham system (the non-interacting system yielding the exact density) is accessible from experimental data, as it can be defined when the density of the system is known.

There are functions closely related to ELF. One has been put forward by Luken and Culberson before the advent of ELF, and has been called the Fermi hole mobility function [11]. They plot the difference $w - w_{\text{hom}}$. Another one is recent, proposed by Schmider and Becke [12], and consists in dropping the term $1/8(|\nabla\rho|2/\rho)$ which reflects the local kinetic energy in the absence of the Pauli principle. It is called LOL (localized orbital locator). In Fig. 6 these quantities are compared for the one-dimensional system having three particles in a box. As most of the experience gathered up to now is with ELF, and there is no evidence yet that there will be any significant improvement by using the different functions, the following discussion will be based on ELF.

3. Limits

The most evident way to analyze ELF is via its graphical representation. We have to take into consideration that even a three-dimensional function is not easy to visualize. In practice, one considers 2D-cuts, or plots of iso-surfaces. Thus, often, several plots have to be shown in order to provide all the significant elements. In order to condense information, one has to find the salient features. Following again Bader [6], it is possible to try to characterize the functions by using the stationary points [8], e.g. to find the positions in space where ELF is maximal, and to use the value of ELF in these points.

Although the maxima have shown to be useful in applications (cf., e.g. [9]) it turns out that there is no absolute scale for ELF. For example, not all maximal values of ELF are close to 1 for the atomic shells (see,

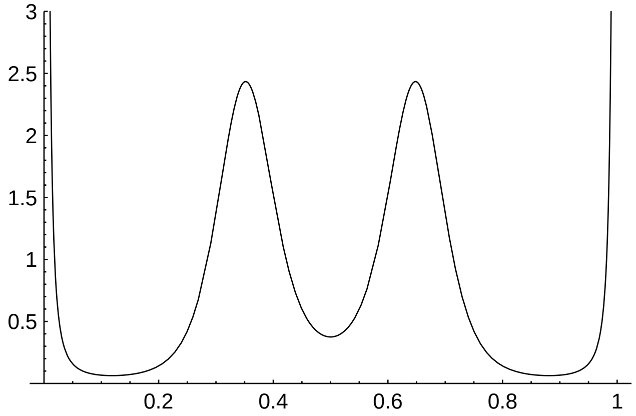

Fig. 4. The ratio between the function *w* (cf. Fig. 3 and text) and the same function defined in a uniform electron gas, as a function of position, showing the regions where the orbitals localize by low values.

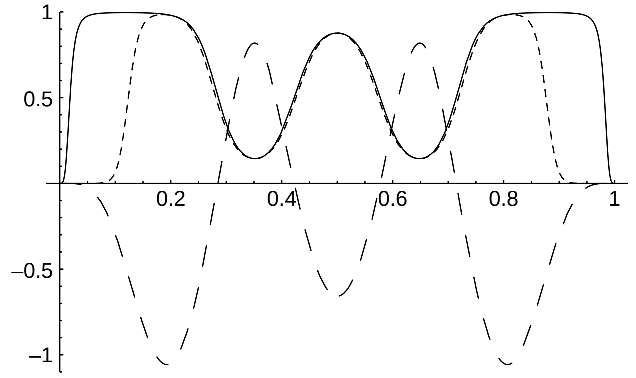

Fig. 6. ELF (full curve, cf. Fig. 5) and functions related to it: LOL (short-dashed curve), and the difference between the Fermi hole mobility function for the given system and the uniform electron gas (divided by 100 to fit into the same graph, long-dashed curve), as a function of the position.

e.g. [1] or [10]). This can be understood from the 'averaging' effect mentioned above: only pure s-shells show values close to 1. Shells where s and p orbitals co-exists, yield values closer to 0.8, while those where s, p and d orbitals are present yield values closer to 0.6 [10]. Furthermore, inner shells penetrate the valence shell and lower the value of ELF (cf. Ref. [4], where the changes in the values of ELF due to the use of pseudopotentials are analyzed). In pseudopotential methods, the presence of different orbitals in the same spatial region is being taken care of by using non-local forms. As functions like ELF are local, it is much more difficult to provide a proper separation. It turns out, however, that ELF works better than many other methods for detecting shells, as for example the Laplacian of the density does not yield a shell structure in some heavier atoms (cf. [6]), while ELF does.

A related effect is the disappearance of the separation between maxima by symmetry. An example is the HCCH molecule, where only a ring (and not three maxima) can be seen between the two C atoms [8]. When symmetry is broken, the three maxima re-appear, but the maxima can be only inconspicuous. A typical example is given by lone pairs, which are often not well separated, reminding of remains of atomic shells (cf. the F lone pairs [8]). A more disturbing feature is that sometimes, when one would expect separated maxima, just a single maximum appear. An example is given by the N_2 molecule, where just one maximum is found between the two N atoms. This is analogous to the merging of close peaks in spectra, and one might expect it to be more important when the peaks are closer (e.g. as N is smaller than C, one might expect it to occur rather in N_2 than in HCCH). In general, one should look into the bifurcation diagram which shows for what range of values the ELF 'peak' exists before merging with another one [18]. When this range is small, one should not attribute much significance to the maxima.

Another feature borrowed from Bader's topological analysis of the density, is the definition of basins[6,8] to define regions of space. This is done by following the gradient path which will lead to an ELF maximum, and collect all points which lead to the same maximum, to a 'basin'. For ELF, which describes electron pairing, one would expect that by integrating the electron density within a basin one gets a number close to 2 (or to a number corresponding to the merged basins, e.g. 8 for the L-shell in atoms). For example, for all functions shown in Fig. 6, the basins are defined on the intervals: (0,0.35),(0.35,0.65) and (0.65,1), yielding by integration of the density in each interval roughly the two electrons.[4] This expectation is quite often fulfilled, but one cannot be too demanding. In addition to reasons evident from the previous discussion about the problem of the disappearance of maxima (and thus 'merging' of basins), there is a deep physical reason which limits the usefulness of any division into basins: quantum mechanically, one can define an average number of electrons in a basin, but this will not be a sharp number in general. To this purpose, one takes the one-body operator which is 1 for a particle in the basin, and 0 otherwise (see, e.g. [16–18]). Its average value gives the number of electrons in the basin. The knowledge of the second-order density matrix allows also the computation of its standard deviation. The latter is in general non-negligible, and can become even significant in the cases when the maxima are only weakly separated [18]. While these results where obtained with ELF, an exploratory calculation shows that the sphere which divides the inner shell of Be from the valence shell in the sense of minimum standard deviation of the number of electrons in the shells is very close to the shell separator given by ELF [19].

4. Conclusions

While ELF has been used—and certainly will continue to be used—with much success for helping chemical understanding, one also must be aware of its limitations, some of which have been discussed in the present paper. While it has simple interpretations (a new one, in terms of localized orbitals has been given here), it is not clear which to take when using many-body wave functions: the different interpretations coincide only for independent particles. Another limitation comes from the local nature of ELF, into which non-local features are projected. Finally, the idea of separating the space into regions containing a pair of electrons has a very important physical limitation: the Heisenberg uncertainty principle. These limitations are not necessarily a handicap for using ELF or similar functions: while we should not give up searching for good tools for chemical understanding, we may ask that some of the pre-quantum mechanics positions of chemistry should be revised.

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