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Electron Localization in Molecules and Solids: The Meaning of ELF

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The orbital underpinnings of the electron localization function (ELF), devised by Becke and Edgecombe, are explored in terms of an interpretation of the dominant term in this expression, $\rho^{-5/3}\sum_i|\nabla\psi_i|^2$. High $\sum_i|\nabla\psi_i|^2$ implies large electronic kinetic energy and electron delocalization. It is shown how this arises in practice through the population of noded wave functions. Such an approach provides an attractive way with which to view electron localization in systems that obey the Hund localization condition, hypervalent and electron-deficient molecules, and metals and insulators. ELF is shown to provide a description of the term "electron localization" that is highly self-consistent when interpreted in terms of nodes and also consistent with many of the present uses of the term.

Introduction

Localization and its antonym, delocalization, are two words with quite a range of meanings in chemistry. For example, "electron precise" molecules and solids such as CF_4 or the sphalerite form of ZnS, containing four-coordinate carbon, zinc, and sulfur, are often considered to be linked by localized bonds, there being four linkages and four s + p orbitals, and a definite Lewis structure may be used to describe these systems. This is the basis of the Hund localization condition.[1] In these cases, "localized" orbitals may be derived from a delocalized molecular orbital picture[2] as, for example, in the classic case of the construction of the four equivalent sp^3 hybrids of methane. The form of such localized functions, though, is perfectly arbitrary; sp^3 hybrids could just as easily be chosen to point at the faces of the tetrahedron as at the corners.

In SF_6 or the rocksalt form of ZnS (the structure found[3] under pressure), where sulfur and zinc are now six-coordinate, there are not enough s/p hybrids to satisfy these six linkages, and so a definite Lewis structure cannot be found to describe these systems and "delocalized" bonds should be expected. Conventional thinking suggests that addition of d orbitals on sulfur in SF_6, for example, should alleviate this problem since six localized d^2sp^3 hybrids result.[4] The question of d orbital involvement in the chemistry of the heavier main group elements has a long history. However, calculation shows[5] that this is not a viable way to get around the problem; the d orbitals are not important. The use of delocalized three-center two-electron bonds,[6] on the other hand, does lead to a good description of the molecule. A similar situation, where there are not enough electrons to satisfy all close atomic contacts with electron pairs, occurs frequently in chemistry. Delocalized bonding over more than two atomic centers is found in many systems, including the benzene π manifold, the singly occupied orbital of triangular H_3^+, and the vast series of boranes and metal cluster compounds. Such electronic situations are often found in solids as well. Furthermore, metals are often envisioned as containing electrons delocalized throughout the solid (so that the electrons are free to move from one side of the sample to another) but insulators as containing localized electrons. The delocalized orbital picture (LCAO) may be used to view all of these examples, but for only a subset (octet systems) is the localized picture a possible alternative.

To attempt to better understand electron localization from a theoretical standpoint, Becke and Edgecombe recently developed the electron localization function (ELF),[7] which has been used to examine localization in atoms, molecules, and solids, especially by Savin and co-workers.[8] As shown in the review,[8] the function has higher values in regions where one expects bonds and lone pairs to be and lower values where one expects more delocalized bonding; plots of ELF correspond quite well to what chemists tend to qualitatively think of as electron localization. Plots of the function are vivid descriptions of regions of localization, as defined by ELF, and give values of localization at each point in space, instead of being centered on atoms, like functions such as Mulliken populations. However, it has remained unclear what information, exactly, is given by ELF. One of the most interesting problems that ELF poses is why it is so independent of the theoretical method used to calculate it. Specifically, it is interesting that plots from extended Hückel calculations, where the pair probability function used to define ELF has little meaning, are almost identical to plots from ab initio calculations.[8]

The purpose of the present paper is to show the connection between ELF and the orbital structure of molecules and solids. We show that if one interprets ELF based upon the nodal properties of the occupied orbitals in a system, instead of in terms of pair probabilities, all of the plots of the function examined thus far are understandable. ELF gives information about the amount of electron density, and the number of nodes, contributed by all of the occupied orbitals to a point in space. Although it does not provide a description of electron localization consistent with all of the present uses of the term, it is still a useful and self-consistent tool with which to view the topic.

Results and Discussion

The Components of ELF. ELF is derived from an earlier idea of Lennard-Jones[9] concerning the pair probability function

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of finding one electron at (x, y, z) and another of the same spin at (x', y', z'). He showed how like-spin electrons occupy separate regions of space, and because this occurs for both up- and down-spin electrons, one can imagine regions of paired electrons. In contrast to the sp^3 hybrids described for methane, the location of these localized electron pairs is not arbitrary.

Becke and Edgecombe[7] showed that regions where the pair probability is high, that is, regions where an electron has a high probability of seeing another electron of the same spin, are regions where the electrons are poorly localized, but where the probability is low the electrons are well-localized. ELF is algebraically defined for a system with σ-spin electron density $\rho_\sigma(x, y, z)$ (where σ can be α- or β-spin) and a set of occupied molecular orbitals, $\{\psi_{i\sigma}\}$ as

$$\mathrm{ELF} = \frac{1}{1 + \left(\dfrac{D_\sigma(x, y, z)}{D_{\sigma,\mathrm{gas}}(x, y, z)}\right)^2} \qquad (1)$$

where

$$D_\sigma(x, y, z)/D_{\sigma,\mathrm{gas}}(x, y, z) = 0.3483\rho_\sigma^{-5/3}\left[\sum_i \left|\nabla\psi_{i\sigma}\right|^2 - \frac{1}{8}\left|\nabla\rho_\sigma\right|^2/\rho_\sigma\right] \qquad (2)$$

D_σ is the leading term in the Taylor expansion of the spherically averaged σ-spin pair probability,[7] and the subscript "gas" refers to the corresponding value for the homogeneous electron gas, the fully-delocalized reference state. Although ELF is defined with ρ and ψ for one spin only, because $\rho_\sigma = 0.5\rho$ for closed-shell systems, this substitution allows ELF to be calculated by methods, such as extended Hückel, that do not explicitly take spin into account.

ELF as defined runs from 0 to 1 and is equal to 0.5 for the homogeneous electron gas. Thus ELF of 1.0 corresponds to perfect localization and ELF of 0.5 to perfect delocalization. Values less than 0.5 are found in areas between concentrations of electron density[10] and will be discussed later.

Some comments are in order concerning ELF and its relationship to other electronic descriptors. Because the negative of the Laplacian of a scalar function shows where values of that function are concentrated or depleted, Bader has been able to show[11] how $-\nabla^2\rho$ may be used to detect where charge density is accumulated and dispersed in a molecule. This function very nicely detects bonds and where one expects to see lone pairs but does not contain any information relating to pairs of electrons. Instead, it shows only regions where charge is accumulated. It has been claimed that ELF and $-\nabla^2\rho$ are "either homeomorphic or...derivable, one from the other".[12] Although it is true that the two functions almost always show the same topology for a given system, there are some cases where the behaviors of the two functions are decidedly different. Figure 1, for example, shows ELF and $-\nabla^2\rho$ plots, at the same scale, through the center of the bonding region of N_2. However, Bader has shown[11] how $-\nabla^2\rho$ is related to the average kinetic and potential energies of a system, and this dependence on kinetic energy is certainly one of the reasons for the great similarities between $-\nabla^2\rho$ and ELF.

Examination of the individual terms in eq 2 is quite revealing. The second term, proportional to the Weiszäcker functional,[12] is what the kinetic energy density at a point in space would be if only one occupied orbital contributed to the electron density at that point. The first term, the actual kinetic energy density at that point, is necessarily greater than or equal to the second term,[12] and in most systems we have studied it is much larger. Thus for the vast majority of systems of chemical interest, the ratio $\sum_i|\nabla\psi_i|^2/\rho^{5/3}$, which appears in eq 2 and hence in the denominator of ELF (eq 1), will be the crucial parameter.

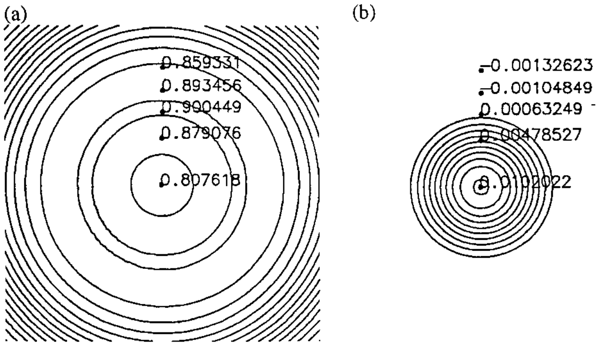


Figure 1. (a) ELF and (b) $-\nabla^2\rho$ plots for N_2 from an extended Hückel calculation. Shown is a 4 Å portion of the plane perpendicular to the N−N bond. Note that the ELF maximum lies outside the central region, while the maximum in $-\nabla^2\rho$ lies at the center of the bond. Contours are shown in intervals of ELF = 0.05 and $-\nabla^2\rho = 0.001$.

The color scheme for plots in this paper follows that in previous publications. Low values of ELF are assigned dark blue, and the colors proceed through the spectrum to green, yellow, orange, and red as ELF increases, leaving white for the highest values. Specifically in this paper, the boundary between yellow and green represents ELF = 0.5, and the boundary between red and white represents ELF = 0.85. Contours on the plots are given in intervals of 0.1 between 0.0 and 0.6 and in intervals of 0.05 between 0.65 and 1.0.

The advantage of discussing ELF in terms of $\sum_i|\nabla\psi_i|^2/\rho^{5/3}$ can be seen in the context of an extended Hückel calculation on H_2, which leads to the ELF of Figure 2a. (The computational details of our studies are given in the Appendix.) The plot in Figure 2a is unlike any published previously in that it contains only a large region of ELF = 1.0. We first try to provide an explanation of this phenomenon in terms of the pair probabilities with which ELF was originally defined.

In its ground state, the two electrons in H_2 are paired in the bonding molecular orbital. The up-spin electron therefore has no probability of encountering another up-spin electron, so the pair probability equals 0 and ELF = 1. The extent of the region of localization is set by an (arbitrary) cutoff at low ρ for the purpose of graphical presentation. (Throughout this paper, ELF is plotted onto the region in which $\rho > 0.001$.) Figure 2b shows ELF for the triplet state of H_2. Now if an electron ventures into the interatomic region, it has a higher probability of encountering a like-spin electron on the other atom, so its conditional pair probability is higher in that region, and thus ELF is lower. Unfortunately, there is a fundamental problem with this analysis: the extended Hückel method does not differentiate between electrons of different spin. In particular, this "triplet" state is simply a state in which each of the bonding and antibonding orbitals has a population of 1. Thus, there must be some other explanation for this result.

The parameter $\sum_i|\nabla\psi_i|^2/\rho^{5/3}$ can be used to understand this phenomenon. Figure 3 shows the classic picture of the bonding and antibonding wave functions of H_2. Notice that the slope of the wave function in the region midway between the nuclei is considerably larger in 3b than in 3a. Since the kinetic energy density of the electrons is directly related to the slope, or gradient, $\nabla\psi_i$, it is easy to see that large contributions to the kinetic energy density occur in the regions between atoms when orbitals with nodes are populated. This increases the denomina-

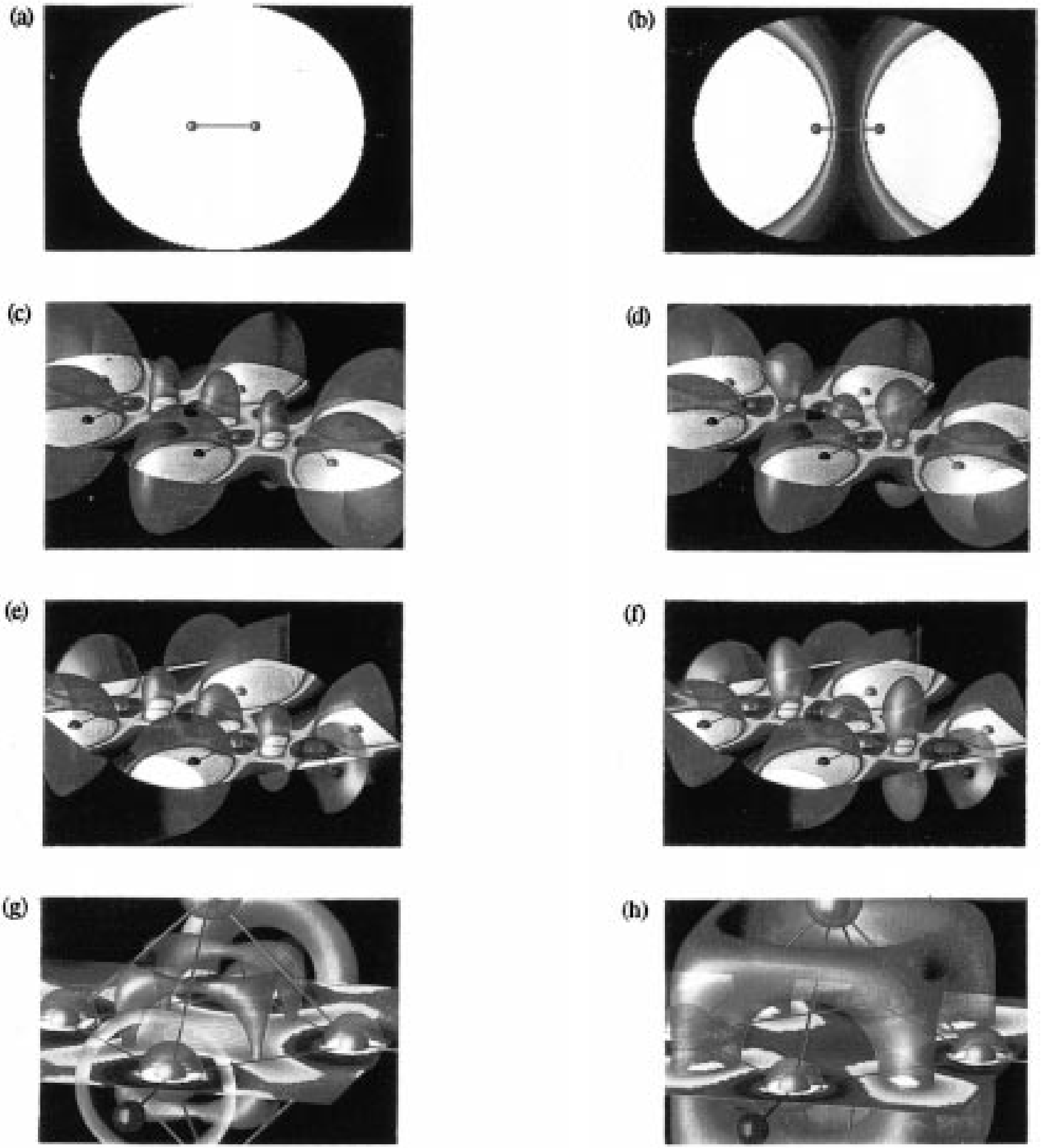


Figure 2. (a) ELF plot for singlet and (b) triplet H_2. (c,d) Calculated ELF plots for butadiene using extended Hückel and (e,f) ab initio methods. The Ψ_1^2 (c,e) and $\Psi_1^2\Psi_2^2$ (d,f) configurations are shown where Ψ_1, Ψ_2 are the deepest-lying pair of π levels. Shown is the molecular plane and the ELF = 0.8 isosurface, inside of which lie all points with ELF ≥ 0.8. (g) ELF plots for the hypothetical $B_6H_6^{10+}$ species and (h) $B_6H_6^{2-}$ from ab initio calculations. Shown is the molecular plane and the ELF = 0.8 isosurface; foreground H's are removed for clarity.

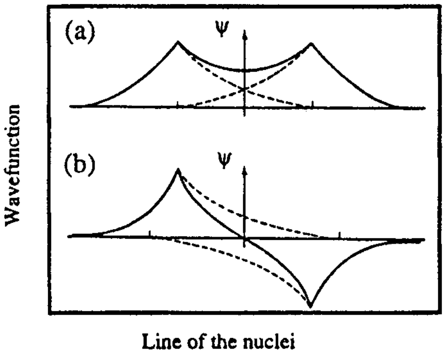


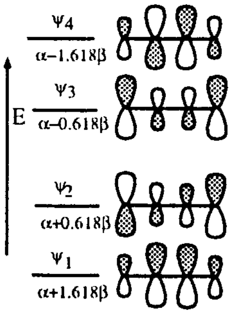
Figure 3. (a) Bonding and (b) antibonding wave functions for H_2. Notice the considerably larger slope of the wave function in (b) than in (a) in the region midway between the nuclei.

tor of ELF, leading to lower values of the function, which correspond to less localization. Indeed, in $^3H_2$, since population of an antibonding orbital with an electron from the bonding orbital excludes density from the interatomic region, the denominator of ELF is decreased even further because ρ is smaller.[13]

In the remainder of this paper, we examine a variety of bonding situations with ELF, to test the applicability of the interpretation of the function based upon the nodal properties of the occupied molecular orbitals of a chemical system.

"Electron Deficient" Molecules. Results analogous to those for ground-state H_2 are found for H_3^+ where, too, a single, nodeless orbital is doubly occupied in the electronic ground state. Thus, although traditionally one would describe the electronic situation in H_3^+,or the π-manifold of $C_3H_3^+$, as delocalized, ELF suggests that the situation is a localized one; that is, high ELF values are found over three centers. Such a result is an example of a situation in which the description of localization given by ELF is different than the common viewpoint.

Figure 2c−f shows ELF for the ψ_1^2 and $\psi_1^2\psi_2^2$ configurations of butadiene (**1**) from both extended Hückel and ab initio calculations. Notice that on population of ψ_2, a π orbital containing a node between the inner pair of atoms, the regions of large ELF values above and below the molecular plane decrease in size here. However, because ρ increases between the outer pairs of atoms, where there are no nodes, the denominator of ELF decreases and the π ELF values increase in these regions. The similarity between the two sets of results reflects the general observation, which has been made previously,[14] that ELF calculated from semiempirical and Hartree−Fock results tends to be nearly the same. This phenomenon is completely in accord with the theory that ELF is dependent on the nodal properties of the occupied orbitals and not the level of theory of the calculation. (Unless, of course, the system is highly correlated and the one-electron picture inappropriate.)



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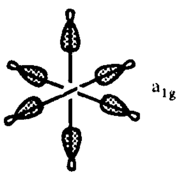
An ELF plot for $B_6H_6^{2-}$ was first displayed in ref 14. In Figure 2g,h we show ELF isosurfaces for both the hypothetical $B_6H_6^{10+}$ species and the $B_6H_6^{2-}$ ion, from ab initio calculations. The former contains filled B−H bonding orbitals plus the single B−B skeletal orbital of a_{1g} symmetry (**2**).[15] Notice that the form of the plot is in accord with the form of this orbital; the absence of B−B nodes inside the cage leads to rather high ELF in this region. (One must keep in mind, however, that there are also lower-energy, occupied B−H orbitals, many of which have nodes through the cage, so the maxima in ELF are not determined solely by the properties of the a_{1g} HOMO.) By the time $B_6H_6^{2-}$ is reached by the filling of orbitals of t_{2g} and t_{1u} symmetry (two examples of which are shown in **3**), a very interesting result is found. From the isosurface of Figure 2h, inside of which lie all ELF values ≥0.8, it is clear that ELF is large on the faces of the octahedron, in accord with the usual description of three-center, two-electron bonds, as noted previously.[14] We can see how this arises from the form of the orbitals of **3**. There are nodes running through the edges of the octahedron (one in each t_{1u} component and two in each t_{2g} component), but electron density is built up in these regions by other orbitals in the triply-degenerate sets as well. Thus $\sum_i|\nabla\psi_i|^2$ and ρ are both large and compete in these regions. In the regions corresponding to the faces of the octahedron, on the other hand, ρ is increased but there are no nodes, so ELF is much larger. Thus, in $B_6H_6^{2-}$ there are regions of large ELF spread over the triangular faces of the octahedron as shown in Figure 2h.



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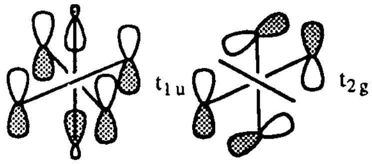

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Metals and Insulators. As noted earlier, insulators are often considered to be composed of localized bonds and metals of delocalized bonds. Diamond is a well-known insulator, but creating a metal by adding electrons to the conduction band, which is composed of orbitals more antibonding between atoms than those in the valence band, leads to a dramatic change in ELF. Figure 4a,b shows the computed ELF plots for both "octet" and electron-doped diamond. Notice that the addition of only 0.75 electrons per atom in the cell eliminates all bonding maxima and that the ELF maximum in the plot drops from 0.95 to 0.72. Furthermore, because electron density is being added to the system but is forbidden by nodes to be between the atoms, the ELF around the atomic centers increases owing to increased ρ in these regions. The ELF of copper is shown in Figure 4c to compare the ELF of a "good" metal, showing extensive delocalization.

Interpreting ELF with nodes leads to an interesting result for full bands. One would expect that because the orbitals at the top of a band have the most nodes possible for the system, an interpretation of ELF based on the nodal properties of the occupied orbitals would make insulators the most delocalized solid systems. We can examine this idea most easily with a one-dimensional chain. Figure 4d−f shows ELF plots of a chain of hydrogen atoms with a unit cell containing 10 atoms. With only two electrons per cell, ELF = 1 everywhere (Figure 4d), both on and between the atoms. This behavior is identical to that already noted for H_2 and is due again to the lack of nodes in the occupied orbital. As more electrons are added to the system, they must occupy more heavily noded orbitals in the band. This causes the ELF values in the interatomic regions to decrease, as can be seen in Figure 4e. When the band is filled, as in Figure 4f, the ELF values in the interatomic regions have dropped below ELF = 0.3, which is well below ELF = 0.5, the "fully delocalized" reference state.

These values are exceedingly low because although density is being added to the system as electrons are put into the bands, the electrons become less and less likely to be in the interatomic regions owing to the great number of nodes in these orbitals. Thus the effect of the large number of nodes on ELF is much greater in the interatomic regions than the counterbalancing effect of increasing the density, so the function values drop as electrons are added. The internuclear nodes also force the electrons that are being added to spend more and more time near the nuclei, so the density in these regions is able to maintain high ELF values. Thus it seems that ELF values below ELF = 0.5 can be interpreted as representing regions where either there is very little electron density, such as between atomic shells,[10] or in regions where the contribution of a great number of nodes to ELF far outweighs the contribution of the density.

Octet and Hypervalent Compounds. In general, as noted earlier, localized orbitals may be derived from a delocalized molecular orbital picture if there are as many doubly filled bonding orbitals as there are "bonds" to be made via these hybrids.[1] However, in SF_6 or rocksalt ZnS, sulfur is six-coordinate and there are not enough s/p hybrids to form six linkages. Thus, one would expect to find delocalized bonds in these systems.

Figure 4g,h shows ELF plots for SF_6 (where one expects to find delocalized bonding) and SF_2 (where localized bonding is expected), resulting from ab initio calculations. On the basis of these expectations, it is quite surprising that the differences in the ELF plots are very minor. In order to understand this,

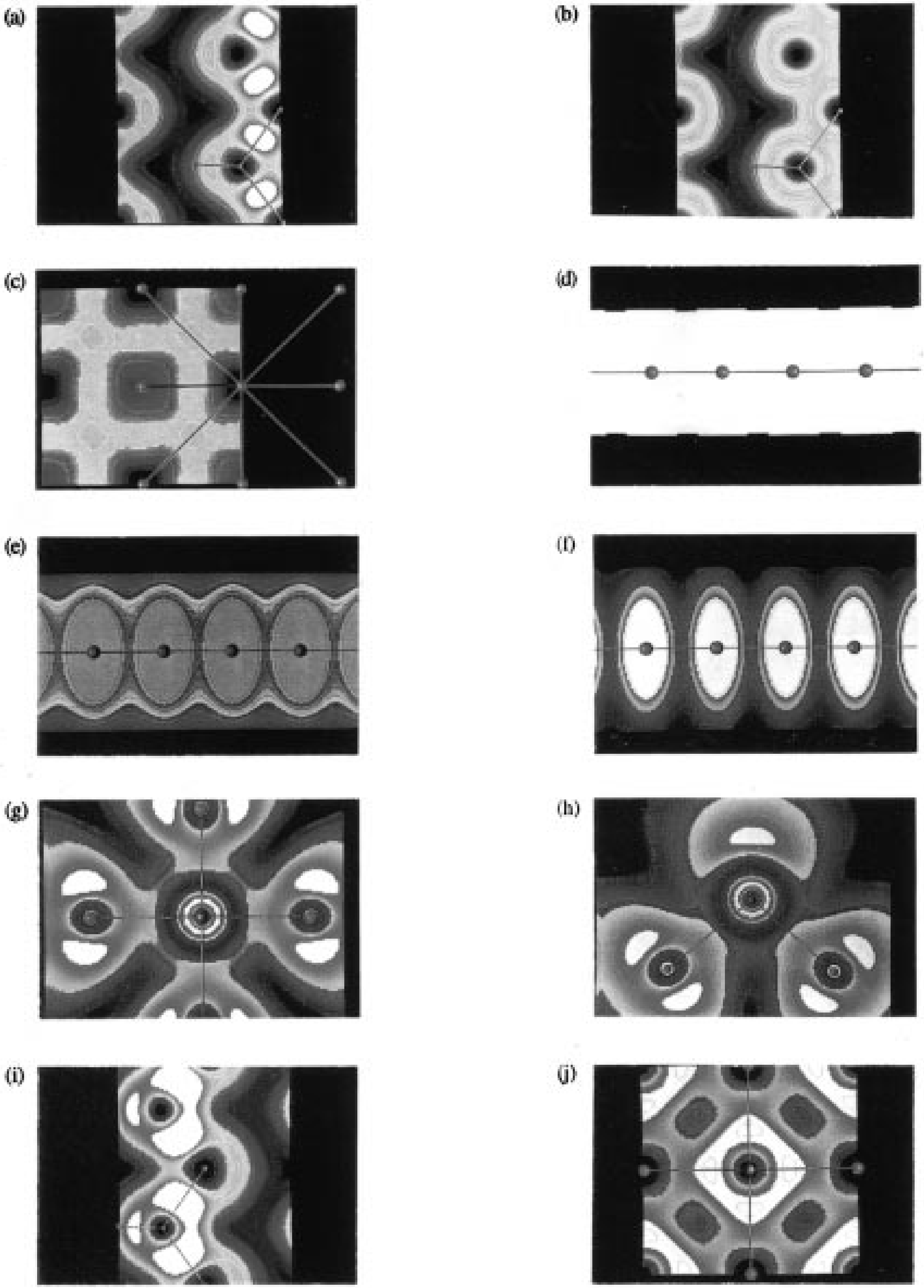
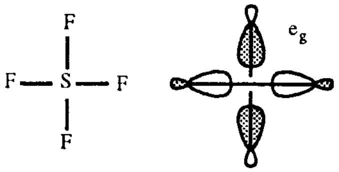


Figure 4. (a) ELF plots (from extended Hückel calculations) before and (b) after doping solid cubic diamond with six electrons per unit cell. Shown is the (110) plane. (c) ELF plot (from extended Hückel calculations) for elemental copper. Plot in the (010) plane. (d) ELF plots (from extended Hückel calculations) of a one-dimensional hydrogen chain, with two electrons per cell, (e) the half-filled band and (f) the filled band. In (d−f), contours are shown at intervals of 0.1 for clarity. (g) ELF plots (from ab initio calculations) for SF_6 and (h) SF_2. (i) ELF plots (from extended Hückel calculations) of solid cubic ZnS [(110) plane], and (j) the rocksalt form of ZnS [(100) plane].

the ELF plots of cations of SF_6 were examined. The S−F bonds were found to have lower, or more delocalized ELF values, until the last two orbitals, a nonbonding e_g set located on the fluorine atoms, were occupied. (One component is shown in **4**.) This pair of orbitals contains nodes between the fluorine atoms but no nodes between sulfur and fluorine. Filling these orbitals, then, leads to increased ρ between sulfur and fluorine and an increase in the number of nodes between fluorine atoms. So, as the last two orbitals are filled, the ELF between sulfur and fluorine increases, and that in the regions between fluorines



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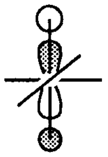
decreases, resulting in a picture very similar to the S−F bonds in SF_2. SF_6, then, can be described as an octet compound of a special type, since one set of ligand orbitals (an e_g pair) cannot interact by symmetry with any of the central atom s or p orbitals. The situation is rather similar electronically to that in the $W(CO)(C_2H_2)_3$ molecule.[16] Here, counting electrons formally leads to a total of 20. Although this is two more than the stable electron count of 18 for transition metal systems, there is one ligand combination (a_2) which by symmetry cannot interact with a central atom s, p, or d orbital.

Calculations[17] that used the method of Boys[18] to localize electrons from a molecular orbital picture also found six well-localized bonds in SF_6. We should note that the Hund localization conditions only apply in fact to rather covalent compounds, i.e., those with a small electronegativity difference between the atoms. For polar compounds, with largely ligand-located orbitals in this case, the traditional picture is therefore not valid, and in this light the results for SF_6 are not unexpected.

Parts i and j of Figure 4 show ELF plots for sphalerite ZnS, which contains four-coordinate sulfur, and for rocksalt ZnS, which contains six-coordinate sulfur. The two structures are quite similar. Both contain a cubic close-packed array of sulfur atoms, with half of the tetrahedral holes occupied by zinc in sphalerite and all of the octahedral holes occupied in rocksalt. However, the ELF plots are very different indeed from those found for SF_6 and SF_2. The large regions of high ELF in sphalerite ZnS decrease both in magnitude and in extent upon a change to the rocksalt arrangement.

This result can again be understood in terms of the nodes of occupied orbitals and the regions of high electron density. Each atom donates one s and three p orbitals to the bonding in both systems. In both structures, there is an occupied, fully bonding combination of s orbitals, which possesses no nodes. Furthermore, each combination that involves a p-π orbital at the corner of a tetrahedron or octahedron will have a nodal plane through the region that is bonding between the corner atom and the central atom. However, in combinations that involve a p orbital at the center of a tetrahedron or an octahedron, and s or p-σ orbitals at the corners, the two structures differ in the number of nodes that pass through bonding regions. In the octahedron, each p orbital on the central atom can form combinations with two of its nearest neighbors, but the interactions between the central atom and its other four nearest neighbors all fall in a nodal plane (one such combination is shown in **5**). In the tetrahedron, on the other hand, this is only the case for two of the three p orbitals on the central atom. There is one combination (**6**) in which the node does not pass through any of the bonds between the central atom and its nearest neighbors. Thus, in these s−p and p−p σ bonds, the atom at the corner is bonding in two of the combinations in the tetrahedron and only in one in the octahedron, and each bond between the central atom and a corner atom falls in only one node in the tetrahedron but two in the octahedron. Because the bonds in the octahedron fall on more nodes and have density in less of the combinations, we would expect the ELF values in the bonding regions in the tetrahedral solid to be higher than those in the octahedral solid, and this is indeed the case.



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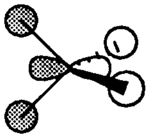

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Conclusions

We have shown for the first time that the electron localization function is based on the nodal properties of the occupied orbitals of a system. Qualitatively, ELF assigns high values to a point in space where there is significant electron density, but few or no nodes pass through the point. It assigns lower values to points that either have little electron density or through which enough nodes from one or more occupied orbitals pass that these nodes can overcome the contribution of the density to ELF at that point. According to this definition, then, electrons are localized at a point in space when there is significant electron density, but few nodes, from all of the occupied orbitals.

This description has been shown to be highly self-consistent both in systems that obey the Hund localization condition and those that do not, such as hypervalent and electron-deficient molecules and solids. It is also self-consistent regardless of the level of theory of the calculation. However, although traditional ideas lead to the viewpoint of delocalized bonding in systems such as triangular H_3^+, ELF values are high in these systems owing to the lack of nodes in the occupied orbitals. ELF thus provides a mathematically precise and readily understandable definition of electron localization, but its results are not always in accord with the large variety of uses of the term “localization” in chemistry.

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Appendix: Computational Details

All tight-binding calculations were performed with the package EHMACC using standard parameters and using the weighted Wolfsberg−Helmholtz approximation.[19] Molecular ab initio calculations were performed with the package GAMESS.[20] The basis sets employed were 6-31G* for the butadiene calculations and 6-311++G** for the B_6H_6 calculations; the McLean/Chandler “triple split” basis set was used for SF_2 and SF_6, which is (12s,9p)/[6s,5p] for sulfur and 6-311G for fluorine.[21] ELF calculations for the extended Hückel output were performed by a package written by Armin Burkhardt and Frank Wagner, kindly supplied by Dr. Thomas Fässler. ELF calculations for the GAMESS output were performed by a modification of the vectorized version of the CUBE[22] program, which is an implementation of Bader’s atoms in molecules approach, following the definition of ELF given in ref 7. The graphic representations were performed using IBM Visualization Data Explorer version 3.1.

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