A topological study of homonuclear multiple bonds between the elements of group 14

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A study of the Electron Localization Function (ELF) for [REER] and [R_2EER_2] (E = Si, Ge, Sn; R = H, CH_3) has been undertaken. It has long been appreciated that the bonding in the heavier group 14 analogues of alkynes and alkenes has a different nature from that in simple carbon-containing molecules. Unlike their carbon analogues they have non-linear and non-planar structures respectively and the EE bonds cannot be described as normal double and triple bonds. There has been much discussion and disagreement concerning the nature of these bonds. We have made an ELF and an AIM study of these molecules to attempt to shed further light on this problem. For all systems the nature of the ligand (H or Me) does not significantly change the bonding picture. Our results reinforce previous experimental and theoretical studies in reproducing the non-linear and non-planar geometries. They show that the ELF results do not lead to quantitative values for the bond orders but indicate that the bond orders are less than three for the REER molecules and less than two for the R_2EER_2 molecules. These conclusions are made more quantitative by the AIM results. We attribute this decrease in bond order to the decreasing ability of these larger and less electronegative elements to attract electrons into the bonding region so that an increasing fraction of the electron density remains as essentially non-bonding or lone pair density.

Introduction

It has long been known that the period 2 elements form many more stable multiple bonds than heavier elements.[1] The C=C and C≡C bonds are the archetypal multiple bonds. It was not until 1989 that the first molecule with a Si=Si double bond was prepared.[2] This molecule, $Si_2\{Mes*\}_4$ (Mes* = 2,4,6-(t-Bu)$_3$-C_6H_2), has four bulky substituents protecting the double bond from attack. An unexpected feature of this molecule is that, unlike C_2H_4, it has a *trans* non-planar geometry with an out-of-plane angle of 18°.

Many other similar molecules (silenes)[3,4] have subsequently been prepared as well as analogous germanium and tin molecules (germenes[5] and stannenes[6]). Many of the silenes have a non-planar *trans* geometry with out-of-plane angles ranging from 0 to 18°.[7,8] The germenes have out-of-plane angles ranging[9–11] from 0 to 42.3° while the stannenes have out-of-plane angles ranging from 29[12] to 41°.[13] *Ab initio* calculations have shown that analogous molecules without the bulky organic ligands such as Si_2Me_4 and Si_2H_4 also have similar *trans*-bent geometries,[14,15] although hydrogen bridged isomers of Si_2H_4, such as HSiHHSiH, have a lower energy. It is well-known that multiple EE bonds are too reactive to be isolated unless protected from attack by bulky ligands. It is generally believed[16] that these bulky ligands play a passive role, serving only to shelter the reactive EE bonds, but not otherwise altering the essential structural and electronic features of the molecule.

There do not appear to be any examples of stable molecules of the type HEEH where E is a period 14 element other than carbon. However, there have been theoretical studies on the molecules HSiSiH,[17] HGeGeH[18] which showed that these molecules have a non-linear *trans* structure. The recent preparation of the anion [Mes*$_2C_6H_3$–Ga≡Ga–C_6H_3Mes*$_2$]$^{2-}$ as its sodium salt which has a non-linear structure with an average Ga–Ga–R angle[19] of 131° has stimulated further interest in the group 14 analogs and the description of the GaGa bond in this molecule as a triple bond led to further lively debate[20] on the nature of multiple bonds between the heavier elements.

A simple explanation for the rarity of examples of multiple bonds between the elements of period 3 and beyond compared to those of period 2 is that only the smallest and most electronegative elements such as C, N and O can exert a sufficiently attractive force to hold four or six electrons in the internuclear bonding region against their mutual electrostatic and Pauli repulsion. The heavier elements attract these electrons less strongly (hence the greater reactivity of their multiply bonded molecules) and it is reasonable to suppose that in these formally multiply-bonded heavier-element molecules some of the potentially bonding electrons remain in the non-bonding region of each atom. Scheme 1 shows possible (very approximate)
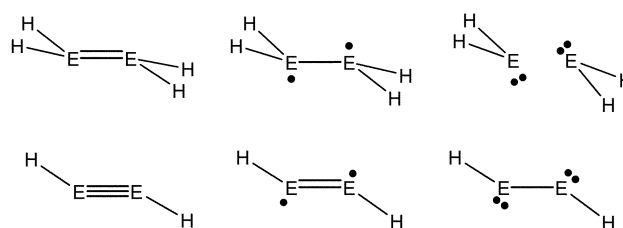
Scheme 1 Proposed resonance structures of H_2EEH_2 and HEEH (E = Si, Sn, Ge).

descriptions of the molecules H_2SiSiH_2 and HGeGeH in which there are respectively one or two non-bonding electrons in the valence shell of each group 14 atom and only a single bond. The presence of the non-bonding electrons is responsible for the non-planarity and non-linearity of these molecules. The results described in this paper provide convincing evidence for this explanation of the geometry.

A number of theoretical studies aimed at providing answers to the two questions (1) Why do these molecules have non-planar and non-linear structures? (2) What is the nature of the formally double and triple bonds? These studies have generally focused on analysis of either canonical[16,21] or localised[22] molecular orbitals (MOs). The canonical MO picture of the

molecules HEEH has been interpreted as describing the bonding between the heavy atoms as due to a π-bond and two distorted "lone-pair" orbitals. These lone pair orbitals are distorted towards the other heavy atom and into the bonding region. Allen et al.[21] calculated a topological bond order[23] based on ρ for trans-MeGeGeMe of 2.1. Xie et al.[22] described the bonding picture in HGaGaH²⁻ from their LMO calculations as two weak dative bonds and a weak π-bond. In the two LMOs described as dative bonds the orbital does not point towards the other atom as found in the classic dative bond in BH_3–NH_3, which resembles a standard σ-bond. Instead the LMOs could perhaps be described as the dative-bond equivalent of a π-bond, although they retain significant lone pair character.

The conclusions of the aforementioned approaches depend on a visual assignment of orbital electron density as bonding or non-bonding. Moreover such interpretation hinges on the selection of certain molecular orbitals, typically the ones of highest energy. A topological approach based on the electron density, on the other hand, such as that of ELF and AIM, always involves the complete wave function. That the interpretation of a MO as bonding or non-bonding is ambiguous is clear from the conflicting conclusions found in the literature. For example, Cotton et al.[16] disagree with Klinkhammer and Schwarz[12] and Xie et al.[22] on this issue for the GaGa bond in molecules with dicoordinated Ga atoms. The determination of the bond order is critically dependent on the number of alleged bonding orbitals. If the "lone pair" character of an MO is ignored, the corresponding bond order will be too high.

The object of the present work was to obtain further understanding of the bonding of these types of molecule by using a topological analysis of ELF and the electron density of the molecules Si_2H_2, Si_2Me_2, Ge_2H_2, Ge_2Me_2, Sn_2H_2, Sn_2Me_2, Si_2H_4, Si_2Me_4, Ge_2H_4, Ge_2Me_4, Sn_2H_4 and Sn_2Me_4.

Brief review of ELF and AIM

A detailed summary of the Electron Localization Function (ELF) and "Atoms in Molecules" (AIM) methods is given in the Appendix; here we provide a very brief overview of the nomenclature used in the two methods. Topological analysis of ELF,[24] which is a simple function of the wave function enables the location of regions of real space (called *basins*) in which pairs of electrons are most likely to be found. In AIM a basin is associated with a nucleus, together constituting an atom. Volume integration over basins yields interesting physical quantities, such as volume, population, fluctuation and relative fluctuation (see Appendix for more detail).

Silvi, Savin and Colonna introduced a nomenclature[25] on the topological connectivity to classify ELF basins. A core basin encloses an ELF attractor at a nucleus.† Core basins are usually totally encapsulated by valence basins, which fill the remaining space. Valence basins are characterized by their synaptic order, which is the number of core basins with which they share a topological boundary or separatrix. Monosynaptic basins are assumed to contain lone pair (non-bonding) density and di- or poly-synaptic basin bonding density. Because hydrogen has no core electrons and no non-bonding electrons the valence protonated basin corresponding to an XH bond is treated as though it were disynaptic. It is convenient to illustrate the typical notation for these ELF basins in water. The core basin is denoted by C(O), the two lone pairs by $V_1(O)$ and $V_2(O)$, and the protonated disynaptic attractors by $V(H_1,O)$ and $V(H_2,O)$. In ELF the order of a bond is defined as one half of the population of the corresponding disynaptic basin.

The AIM bond order, denoted by B_{AB}, gives the number of electron pairs shared between the two atoms A and B. In other

words it is a measure of the extent to which the electrons in A are delocalized into atom B and *vice versa*.[26] Similarly the "ELF contribution analysis" is a measure of the sharing of electron pairs between ELF basins.

Computational details

All wave functions and their corresponding densities have been obtained with the GAUSSIAN98 suite of codes.[27] The B3LYP hybrid density functional[28] has been employed throughout. We have used the 6-31G*[29] and cc-pVDZ[30–32] sets for all atoms except Sn, for which the (28s,23p,17d)/[5s,4p,2d] well tempered basis set of Huzinaga et al.[33,34] was used for single point evaluation of the density and the LANL2DZ[35] effective core potential was employed for the geometry optimisation. Results with the two different basis sets are in general very close and we have restricted presentation of data to that found using the cc-pVDZ basis set, unless there is a qualitative difference, where we show both sets of results (details in Results and discussion). Geometries were obtained using analytical gradient techniques and all REER systems were restricted to retain C_{2h} symmetry.

The assignment of the ELF basins and the subsequent integration of the electron density over them was performed using the TopMoD code.[36] Due to numerical grids employed in the TopMod code slight artifactual asymmetries appear in the integrated data, which is why they are quoted with a minimal number of significant figures. Very fine grids would remove these discrepancies but the required additional cost is not justified since the extra precision would not alter our conclusions.

The topological bond orders B_{AB} were calculated with MORPHY01,[37] which was also used to confirm the number and position of the ELF attractors. The ELF isosurface plots were generated with SciAn.[38]

Results and discussion

C_2H_2

The nature of the bonding in ethyne is relevant to this study in order to draw comparisons with the results for the heavier group 14 elements. The bonding in ethyne is well understood, consisting of a σ-bond and two degenerate π-bonds in the molecular orbital picture. In terms of ELF the CC bond in ethyne is found to have a single toroidal disynaptic basin containing six electrons. This description of the bonding is in accord with the Linnett double quartet model,[39,40] in which each of the six CC bonding electrons has a most probable location somewhere on a circle surrounding the bond axis, see Fig. 1. There is no formation of bonding pairs as electrostatic
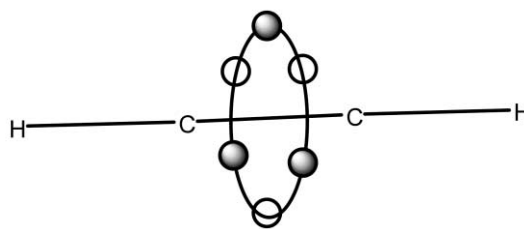

Fig. 1 Linnett model of C_2H_2, α and β electrons are represented by filled and open circles respectively.

repulsion keeps opposite spin electrons apart, mirrored in the toroidal basin in ELF. The picture of the bonding differs from the conventional Lewis structure, which implies that there are three bonding *pairs* of electrons.

Si_2H_2 and Si_2Me_2

Table 1 shows the calculated E bond lengths for all the molecules. The larger cc-pVDZ basis set predicts somewhat longer

Table 1 Bond lengths (Å) for REER and R_2EER_2, R = H,CH_3 and E = Si,Ge,Sn, and H_3SiSiH_3 at the B3LYP/6-31G* and B3LYP/cc-pVDZ levels

	r_e(EE)/6-31G*	r_e(EE)/cc-pVDZ
Si_2H_2	2.11	2.11
Si_2Me_2	2.12	2.13
Ge_2H_2	2.18	2.23
Ge_2Me_2	2.20	2.25
Sn_2H_2[a]	2.64	2.64
Sn_2Me_2[a]	2.66	2.66
Si_2H_4	2.18	2.18
Si_2Me_4	2.19	2.18
Ge_2H_4	2.26	2.31
Ge_2Me_4	2.29	2.34
Sn_2H_4[a]	2.77	2.77
Sn_2Me_4[a]	2.79	2.79
Si_2H_6	2.35	2.36

[a] All compounds containing Sn involved the LANL2DZ[35] effective core potential for the geometry optimizations.

bond lengths except for Si_2Me_4. Both basis sets predict the EE bond lengths in the methylated compounds to be slightly longer. The calculated EE bond lengths in the REER systems are invariably shorter than in their R_2EER_2 counterparts. In particular the Si–Si bond length in Si_2H_2 is 0.07 Å shorter than in Si_2H_4 and 0.24 Å shorter than in Si_2H_6, a total shrinkage of about 10%. The relative bond length shortening in the series ethane, ethene, ethyne amounts to about 20%.

Figs. 2a and 2b show the $\eta = 0.7$ ELF isosurfaces for the HSiSiH and MeSiSiMe molecules. This isosurface has the shape of the torus observed in HCCH but elongated and with its long axis tilted with respect to the bond axis. At high η values this basin splits into four monosynaptic V(Si) basins and two disynaptic V(Si,Si) basins each containing approximately one electron giving the expected total of six electrons (see Table 2). This splitting into separate basins is a consequence of the reduction of the symmetry from linear. According to the conventional ELF analysis the monosynaptic basins are regarded as non-bonding and the disynaptic basins as bonding. This result is consistent with the simple bonding model consisting of one "split" single bond (two bent half bonds) and two lone pairs. The relation of this description of the bonding to the Linnett description of the triple bond in ethyne is shown in Fig. 3. Here we see that the ring of six electrons is tilted so that two of the electrons come closer to one Si atom and another two electrons closer to the other Si atom, forming two approximate pairs and leaving two single bonding electrons.
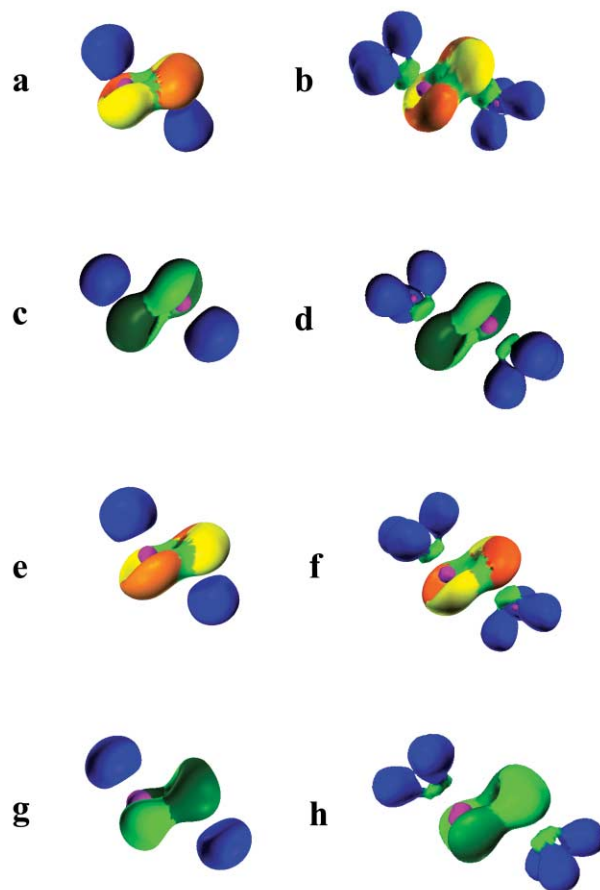

Fig. 2 The $\eta = 0.7$ ELF isosurfaces for the REER systems at two levels of theory. Colour legend: Core basin (magenta), valence protonated (blue), valence disynaptic (light green and dark green) and valence monosynaptic (orange and yellow). (a) Si_2H_2 at 6-31G* level, (b) Si_2Me_2 at 6-31G* level, (c) Ge_2H_2 at cc-pVDZ level, (d) Ge_2Me_2 at cc-pVDZ level, (e) Ge_2H_2 at 6-31G* level, (f) Ge_2Me_2 at 6-31G* level, (g) Sn_2H_2 at 6-31G* level (except for Sn), (h) Sn_2Me_2 at 6-31G* level (except for Sn).

Fig. 3 Linnett model of Si_2H_2, α and β electrons are represented by filled and open circles respectively.

Table 2 Basin volumes (arb. units), populations, standard deviations, relative fluctuations and contributions of other basins (%), for Si_2H_2 and Si_2Me_2

Basin	Volume	N_i	$\sigma(N_i)$	$\lambda(N_i)$	Contribution analysis
Si_2H_2					
$V(Si_1)$	127	1.0	0.7	0.7	$V(H_1,Si_1)$ 10%, $V(Si_2)$ 11%, $V(Si_1,Si_2)$ 15%
$V(Si_1)$	131	1.0	0.7	0.7	$V(H_1,Si_1)$ 11%, $V(Si_2)$ 11%, $V(Si_1,Si_2)$ 14%
$V(Si_2)$	127	1.0	0.7	0.7	$V(H_2,Si_2)$ 10%, $V(Si_1)$ 12%, $V(Si_1,Si_2)$ 15%
$V(Si_2)$	131	1.0	0.7	0.7	$V(H_2,Si_2)$ 11%, $V(Si_1)$ 11%, $V(Si_1,Si_2)$ 14%
$V(Si_1,Si_2)$	37	0.9	0.7	0.7	$V(Si_1)$ 15%, $V(Si_2)$ 17%, $V(Si_1,Si_2)$ 11%
$V(Si_1,Si_2)$	40	1.0	0.7	0.7	$V(Si_1)$ 15%, $V(Si_2)$ 15%, $V(Si_1,Si_2)$ 10%
Si_2Me_2					
$V(Si_1)$	121	1.0	0.7	0.7	$V(Si_1)$ 11%, $V(Si_2)$ 11%, $V(Si_1,Si_2)$ 15%
$V(Si_1)$	123	1.0	0.7	0.7	$V(Si_2)$ 11%, $V(Si_1)$ 11%, $V(Si_1,Si_2)$ 15%
$V(Si_2)$	121	1.0	0.7	0.7	$V(Si_1)$ 11%, $V(Si_2)$ 11%, $V(Si_1,Si_2)$ 15%
$V(Si_2)$	123	1.0	0.7	0.7	$V(Si_2)$ 11%, $V(Si_1)$ 11%, $V(Si_1,Si_2)$ 15%
$V(Si_1,Si_2)$	43	1.0	0.7	0.7	$V(Si_2)$ 16%, $V(Si_1)$ 16%, $V(Si_1,Si_2)$ 10%
$V(Si_1,Si_2)$	45	1.1	0.7	0.7	$V(Si_1)$ 15%, $V(Si_2)$ 15%, $V(Si_1,Si_2)$ 10%

The weaker attraction of the Si atom compared to the C atom towards its valence shell electrons means that not all six potential bonding electrons are drawn completely into the bonding region. In fact, according to ELF, if the disynaptic basins represent bonding electrons and monosynaptic basins represent non-bonding electrons then there are two non-bonding pairs and two bonding electrons as illustrated in Figs. 2a and 2b. However, the SiSi bond in Si_2H_2 is shorter than in Si_2H_4, which in turn is appreciably shorter than the SiSi bond in Si_2H_6 (Table 1), suggesting that the former cannot be a single bond, assuming that bond order is related to bond length. Thus a naïve interpretation of the ELF picture is not satisfactory. The monosynaptic basins extend significantly into what is usually considered to be the bonding region suggesting that these basins have both bonding and non-bonding character, which would account for the SiSi bond being shorter than a SiSi single bond. Clearly, as a result of the smaller electronegativity of Si compared to C there is a tendency for some of the potentially bonding electrons to remain associated with the Si atoms as non-bonding electrons rather than being attracted into the bonding region, which is why the molecule is not linear. A very similar picture is given by the Linnett model shown in Fig. 3. As the ring of six electrons is tilted out of being perpendicular to the internuclear axis four of the electrons take on more of the character of two lone pairs.

The volumes, populations, standard deviations, relative fluctuations and the contributions from other basins towards that fluctuation for Si_2H_2 and Si_2Me_2 are given in Table 2. The two disynaptic basins each with a population of approximately one electron and symmetric fluctuation contributions from both silicon atoms, and a small volume indicate a bonding interaction. The four monosynaptic basins are non-bonding in character, though the strong fluctuations with the monosynaptic basins associated with the other silicon atoms imply some bonding character.

In terms of conventional Lewis structures the best description of the bonding would be that it is a single bond that has a small amount of triple bond character resulting from the formal "lone pairs" giving a bond that is intermediate between a single and a triple bond. However, we note that the Linnett model gives a somewhat more satisfactory picture. With increasing size and decreasing electronegativity the electrons in the valence shell of an atom in a molecule become increasingly less localized and it becomes increasingly difficult to describe these electrons clearly as either bonding or non-bonding. We cannot therefore find the exact number of bonding electrons. The populations of the two disynaptic basins indicate that the bond order is approximately one but the apparent additional contribution of the monosynaptic basin electrons to the bonding implies that the bond order is greater than one but clearly much less than three.

Ge_2H_2 and Ge_2Me_2, Sn_2H_2 and Sn_2Me_2

Figs. 2c and 2d show the $\eta = 0.7$ ELF isosurfaces for the HGeGeH and MeGeGeMe molecules calculated at the B3LYP/cc-pVDZ level. The corresponding integrated properties are given in Table 3. In these molecules the two disynaptic basins and the four monosynaptic basins observed in the corresponding Si molecules have been replaced by four disynaptic basins each containing 1.5 electrons for a total of six electrons. However, the overall appearance of the toroidal basin is very similar to that in the Si molecules and the positions of the attractors and large basin volumes strongly suggest that they have considerable non-bonding character and only a small amount of bonding character. Again we see the difficulty of distinguishing between bonding and non-bonding electrons and therefore of determining the bond order of these bonds. Qualitatively all XEEX molecules have a number of bonding electrons that decreases from three in XCCX molecules and a

number of non-bonding electrons that increases from zero for XCCX.

The $\eta = 0.7$ isosurface for HGeGeH and MeGeGeMe obtained at B3LYP/6-31G* level are shown in Figs. 2e and 2f and the integrated properties in Table 3. The results at this level are analogous to those seen for the Si molecules, *i.e.* two disynaptic and four monosynaptic basins in a toroidal arrangement, each containing approximately one electron. The differences in ELF observed between the two basis sets illustrate the difficulties associated with a simple assignment of density as either bonding or non-bonding.

The results for the Sn molecules are given in Table 4 and Figs. 2g and 2h. They are very similar to the analogous Ge molecules at the B3LYP/cc-pVDZ level. The only slight differences between Sn and Ge molecules are that the Sn disynaptic basins have a larger volume, which indicates greater non-bonding character.

Si_2H_4 and Si_2Me_4

The results for these molecules are given in Table 5. Figs. 4a and 4b illustrate the ELF isosurfaces at the B3LYP/6-31G* level.

Fig. 4 The $\eta = 0.7$ ELF isosurfaces for the R_2EER_2 systems at two levels of theory. Colour legend as in Fig. 2. (a) Si_2H_4 at 6-31G* level, (b) Si_2Me_4 at 6-31G* level, (c) Si_2H_4 at cc-pVDZ level, (d) Si_2Me_4 at cc-pVDZ level, (e) Ge_2H_4 at 6-31G* level, (f) Ge_2Me_4 at 6-31G* level, (g) Sn_2H_4 at 6-31G* level (except for Sn), (h) Sn_2Me_4 at 6-31G* level (except for Sn).

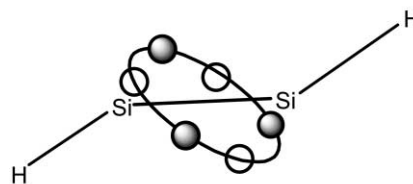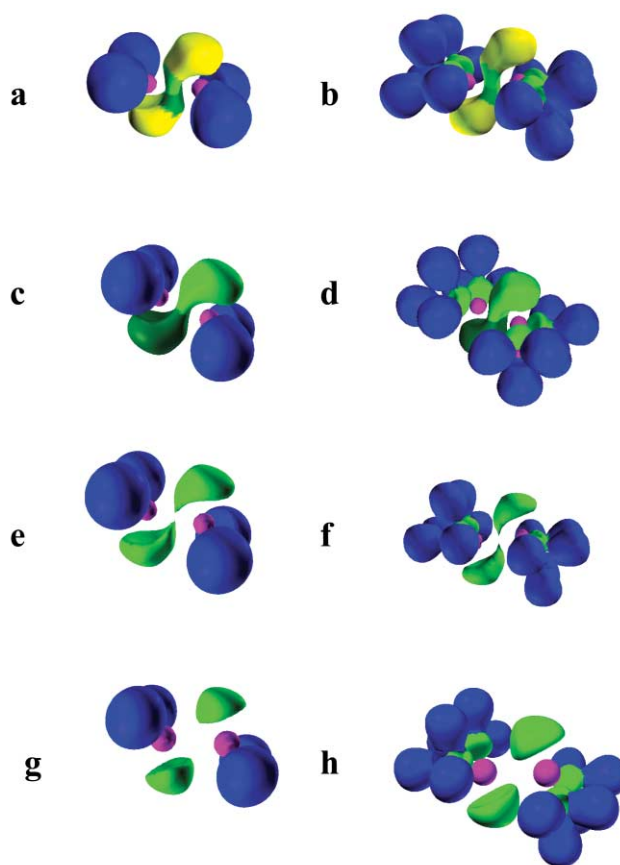Si_2H_4 and Si_2Me_4 have a monosynaptic non-bonding basin on each Si atom, each having a population of one electron and two smaller disynaptic bonding basins each with a population of one electron. This can be interpreted as indicating a single bond or, as in Si_2H_2 and Si_2Me_2, two half bonds (a "π" bond in orbital terms), one on each side of the molecular axis and a single non-bonding electron on each Si atom. This description corresponds approximately to the structure shown in Scheme 1. Again the monosynaptic "lone pair" basins extend into the

Table 3 Basin volumes (arb. units), populations, standard deviations, relative fluctuations and contributions of other basins (%), for Ge_2H_2 and Ge_2Me_2

Basin	Volume	N_i	$\sigma(N_i)$	$\lambda(N_i)$	Contribution analysis
Ge_2H_2	cc-pVDZ				
$V(Ge_1,Ge_2)$	151	1.7	1.1	0.7	$C(Ge_2)$ 20%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1,Ge_2)$	152	1.6	1.1	0.7	$C(Ge_1)$ 19%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1,Ge_2)$	151	1.7	1.1	0.7	$C(Ge_2)$ 20%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1,Ge_2)$	153	1.7	1.1	0.7	$C(Ge_2)$ 19%, $V(Ge_1,Ge_2)$ 13%
Ge_2Me_2	cc-pVDZ				
$V(Ge_1,Ge_2)$	148	1.7	1.1	0.7	$C(Ge_2)$ 20%, $V(Ge_1,Ge_2)$ 12%
$V(Ge_1,Ge_2)$	147	1.6	1.1	0.7	$C(Ge_1)$ 20%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1,Ge_2)$	151	1.7	1.2	0.7	$C(Ge_1)$ 20%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1,Ge_2)$	153	1.8	1.2	0.7	$C(Ge_2)$ 20%, $V(Ge_1,Ge_2)$ 12%
Ge_2H_2	6-31G*				
$V(Ge_1)$	101	1.0	0.8	0.8	$C(Ge_1)$ 21%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1)$	104	1.0	0.8	0.8	$C(Ge_1)$ 22%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_2)$	100	1.0	0.7	0.8	$C(Ge_2)$ 22%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_2)$	104	1.0	0.8	0.8	$C(Ge_2)$ 22%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1,Ge_2)$	38	1.1	0.8	0.7	$C(Ge_2)$ 12%, $C(Ge_2)$ 12%, $V(Ge_1)$ 12%, $V(Ge_2)$ 12%
$V(Ge_1,Ge_2)$	39	1.1	0.8	0.7	$C(Ge_2)$ 12%, $C(Ge_2)$ 12%, $V(Ge_1)$ 12%, $V(Ge_2)$ 12%
Ge_2Me_2	6-31G*				
$V(Ge_1)$	113	1.1	0.9	0.8	$C(Ge_1)$ 22%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1)$	115	1.1	0.9	0.8	$C(Ge_1)$ 21%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_2)$	112	1.1	0.9	0.8	$C(Ge_2)$ 22%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_2)$	115	1.1	0.9	0.8	$C(Ge_2)$ 21%, $V(Ge_1,Ge_2)$ 13%
$V(Ge_1,Ge_2)$	58	1.2	0.9	0.7	$C(Ge_1)$ 12%, $C(Ge_2)$ 12%, $V(Ge_1)$ 13%, $V(Ge_2)$ 13%
$V(Ge_1,Ge_2)$	51	1.1	0.8	0.7	$C(Ge_1)$ 12%, $C(Ge_2)$ 12%, $V(Ge_1)$ 13%, $V(Ge_2)$ 13%

Table 4 Basin volumes (arb. units), populations, standard deviations, relative fluctuations and contributions of other basins (%), for Sn_2H_2 and Sn_2Me_2

Basin	Volume	N_i	$\sigma(N_i)$	$\lambda(N_i)$	Contribution analysis
Sn_2H_2					
$V(Sn_1,Sn_2)$	204	1.5	1.1	0.7	$C(Sn_2)$ 23%, $V(Sn_1,Sn_2)$ 12%
$V(Sn_1,Sn_2)$	209	1.6	1.1	0.7	$C(Sn_1)$ 23%, $V(Sn_1,Sn_2)$ 11%
$V(Sn_1,Sn_2)$	205	1.5	1.1	0.7	$C(Sn_1)$ 23%, $V(Sn_1,Sn_2)$ 12%
$V(Sn_1,Sn_2)$	210	1.6	1.1	0.7	$C(Sn_2)$ 23%, $V(Sn_1,Sn_2)$ 11%
Sn_2Me_2					
$V(Sn_1,Sn_2)$	189	1.6	1.1	0.7	$C(Sn_2)$ 23%, $V(Sn_1,Sn_2)$ 11%
$V(Sn_1,Sn_2)$	192	1.6	1.1	0.7	$C(Sn_1)$ 23%, $V(Sn_1,Sn_2)$ 11%
$V(Sn_1,Sn_2)$	198	1.7	1.1	0.7	$C(Sn_1)$ 23%, $V(Sn_1,Sn_2)$ 11%
$V(Sn_1,Sn_2)$	195	1.7	1.1	0.7	$C(Sn_2)$ 23%, $V(Sn_1,Sn_2)$ 11%

Table 5 Basin volumes (arb. units), populations, standard deviations, relative fluctuations and contributions of other basins (%), for Si_2H_4 and Si_2Me_4

Basin	Volume	N_i	$\sigma(N_i)$	$\lambda(N_i)$	Contribution analysis
Si_2H_4	cc-pVDZ				
$V(Si_1,Si_2)$	174	2.0	1.0	0.5	$V(Si_1,Si_2)$ 17%
$V(Si_1,Si_2)$	175	2.0	1.0	0.5	$V(Si_1,Si_2)$ 17%
Si_2Me_4	cc-pVDZ				
$V(Si_1,Si_2)$	153	2.0	1.0	0.5	$V(Si_1,Si_2)$ 16%
$V(Si_1,Si_2)$	154	2.1	1.0	0.5	$V(Si_1,Si_2)$ 15%
Si_2H_4	6-31G*				
$V(Si_2)$	142	1.1	0.7	0.7	$V(Si_1)$ 11%, $V(Si_1,Si_2)$ 15%
$V(Si_1)$	142	1.0	0.7	0.7	$V(Si_2)$ 11%, $V(Si_1,Si_2)$ 15%
$V(Si_1,Si_2)$	20	0.9	0.6	0.7	$V(Si_2)$ 19%, $V(Si_1,Si_2)$ 17%
$V(Si_1,Si_2)$	20	0.9	0.6	0.7	$V(Si_1)$ 18%, $V(Si_1,Si_2)$ 17%
Si_2Me_4	6-31G*				
$V(Si_2)$	137	1.3	0.8	0.7	$V(Si_1)$ 10%, $V(Si_1,Si_2)$ 14%
$V(Si_1)$	137	1.3	0.8	0.7	$V(Si_2)$ 10%, $V(Si_1,Si_2)$ 14%
$V(Si_1,Si_2)$	17	0.8	0.6	0.8	$V(Si_1)$ 23%, $V(Si_1,Si_2)$ 17%
$V(Si_1,Si_2)$	18	0.8	0.6	0.7	$V(Si_2)$ 22%, $V(Si_1,Si_2)$ 16%

Table 6 Basin volumes (arb. units), populations, standard deviations, relative fluctuations and contributions of other basins (%), for Ge_2H_4 and Ge_2Me_4

Basin	Volume	N_i	$\sigma(N_i)$	$\lambda(N_i)$	Contribution analysis
Ge_2H_4					
$V(Ge_1,Ge_2)$	178	2.2	1.3	0.6	$C(Ge_2)$ 17.7%, $V(Ge_1,Ge_2)$ 13.6%
$V(Ge_1,Ge_2)$	179	2.2	1.3	0.6	$C(Ge_2)$ 18.1%, $V(Ge_1,Ge_2)$ 13.6%
Ge_2Me_4					
$V(Ge_1,Ge_2)$	166	2.3	1.4	0.6	$C(Ge_2)$ 18.1%, $V(Ge_1,Ge_2)$ 13.0%
$V(Ge_1,Ge_2)$	167	2.3	1.4	0.6	$C(Ge_1)$ 18.1%, $V(Ge_1,Ge_2)$ 12.9%

bonding region so it is difficult to give a value for the bond order except to say that it is somewhat greater than one.

Figs. 4c and 4d show the ELF isosurfaces for Si_2H_4 and Si_2Me_4 at the B3LYP/cc-pVDZ level. Each bonding basin observed before at the B3LYP/6-31G* level is merged with a non-bonding basin to give just two disynaptic basins, each containing two electrons. Again it is difficult to distinguish between the non-bonding and bonding electrons in these molecules. The four potential bonding electrons retain considerable non-bonding character and the presence of this non-bonding density on the two Si atoms accounts for the non-planarity of the molecule.

The disynaptic basins at the B3LYP/6-31G* level have a small volume indicating true bonding character, in contrast to monosynaptic (non-bonding) basins which are considerably larger. This is in contrast to the picture at the cc-pVDZ level where the disynaptic basins have very large volumes, approximately equal to the sum of the mono- and di-synaptic basins seen at the 6-31G* level. The fluctuation contributions to these basins are dominated by those from a single monosynaptic basin. This is in contrast to the equal contributions seen in Si_2R_2 systems from the monosynaptic basins associated with each Si atom, but should still be interpreted as indicating a single bond (or two half bonds). Again it appears that the monosynaptic basins extend into the bonding regions at the B3LYP/6-31G* level, and the disynaptic basins extend into the non-bonding region at the cc-pVDZ level, thus making it difficult to assign a bond order directly from the ELF populations and basin synaptic orders, other than stating that it is somewhat greater than one.

Ge_2H_4 and Ge_2Me_4

The results for these molecules are given in Table 6 and Figs. 4e and 4f. Both these molecules have two disynaptic basins but the monosynaptic basins on either Ge are not observed, as they were for the analogous Si molecules at the B3LYP/6-31G* level. A conventional interpretation of the ELF basins would be that the two disynaptic basins are bonding basins each with a population of two electrons, corresponding to a conventional double bond. However, the shape of these basins, the positions of their attractors (see Fig. 5) and their large volumes are not in accord with this interpretation as they indicate that each basin also has a considerable non-bonding character. Again it is difficult to distinguish between bonding and non-bonding density. The ELF description corresponds to a Lewis diagram in which there are two electron pairs in positions intermediate between a bonding position and a non-bonding position, shown in Scheme 1.

We could think of two GeH_2 molecules approaching each other and beginning to share their non-bonding pairs but because of the large size of the Ge atoms they are not attracted strongly enough to fully overcome the electrostatic and Pauli repulsion between them so that they do not both completely occupy the bonding region but they take up most probable equilibrium positions in which they have both a bonding and a non-bonding role. In their non-bonding role these electrons prevent
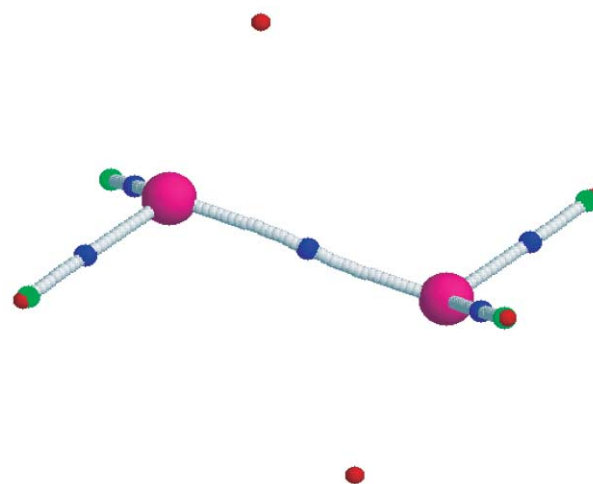

Fig. 5 ELF maxima (red spheres) superimposed on the molecular graph (connectivity scheme between critical points in ρ) for Ge_2H_4 at cc-pVDZ level. Colour legend: Ge (large magenta spheres), maxima in ρ (green), bond critical points (saddle) (blue).

the molecule from adopting a planar conformation as in all the other molecules we have considered.

The integrated properties for the Ge_2R_4 molecules are given in Table 6. The two disynaptic basins contain around two electrons. However, from Figs. 4e and 4f it is obvious that the electrons in these basins cannot be considered to be purely bonding in nature due to their extension into clearly non-bonding regions, which is supported by the large volumes of the basins. The fluctuation contributions also indicate a strong non-bonding character, showing strong asymmetric delocalisation with the core basins of one or more Ge nuclei.

Sn_2H_4 and Sn_2Me_4

The results for these molecules are given in Table 7 and Figs. 4g and 4h. In these molecules the two disynaptic basins each having a population of two electrons closely resemble lone pair basins in position, shape and size. These molecules could be considered to consist of two $:SnX_2$ molecules held together by two unusual bent dative bonds formed by the donation of a lone pair of one SnX_2 molecule into the incomplete valence shell of the other SnX_2 molecule.

As with the Ge compounds the two disynaptic basins contain approximately two electrons (Table 7). Again it is obvious that the electrons in these basins cannot be considered to be purely bonding in nature due to their extension into clearly non-bonding regions, and also because of their large volumes. The fluctuation contributions also indicate a strong non-bonding character, showing strong asymmetric delocalisation with the core basins of either Sn nucleus. The "lone-pair" character of these basins is more pronounced for Sn than for Ge.

Topological bond order

Table 8 shows topological bond orders for all molecules at B3LYP/cc-pVDZ level. These supplementary data consistently

Table 7 Basin volumes (arb. units), populations, standard deviations, relative fluctuations and contributions of other basins (%), for Sn_2H_4 and Sn_2Me_4

Basin	Volume	N_i	$\sigma(N_i)$	$\lambda(N_i)$	Contribution analysis
Sn_2H_4					
$V(Sn_1,Sn_2)$	264	2.2	1.4	0.6	$C(Sn_2)$ 22%, $V(Sn1,Sn2)$ 12%
$V(Sn_1,Sn_2)$	265	2.2	1.4	0.6	$C(Sn_1)$ 22%, $V(Sn1,Sn2)$ 12%
Sn_2Me_4					
$V(Sn_1,Sn_2)$	262	2.4	1.4	0.6	$C(Sn_1)$ 21%, $V(Sn_1,Sn_2)$ 12%
$V(Sn_1,Sn_2)$	262	2.4	1.4	0.6	$C(Sn_2)$ 21%, $V(Sn_1,Sn_2)$ 12%,

Table 8 Topological bond orders for REER and R_2EER_2, R = H, CH_3 and E = Si, Ge, Sn calculated at the B3LYP/cc-pVDZ level

	B_{EE}
$Si_2H_2{}^a$	2.0
Si_2Me_2	1.9
Ge_2H_2	2.0
Ge_2Me_2	2.0
$Sn_2H_2{}^b$	1.9
$Sn_2Me_2{}^b$	1.9
Si_2H_4	1.2
Si_2Me_4	1.2
Ge_2H_4	1.4
Ge_2Me_4	1.3
$Sn_2H_4{}^b$	1.2
$Sn_2Me_4{}^b$	1.2

[a] Bond order calculations were only possible after removal of non-nuclear attractors in the gradient vector field of ρ by slightly elongating the SiSi bond length to 2.2 Å in Si_2R_2 and to 2.4 Å in Si_2R_4. [b] All compounds containing tin have used the LANL2DZ effective core potential for geometry optimizations.

show that the REER systems have an EE bond order near two, and that the R_2EER_2 systems have an EE bond order between 1.2 and 1.4. These values confirm, independently from ELF, that the bond order is substantially less than one would expect from naïve Lewis structures, i.e. a bond order of three for REER and of two for R_2EER_2. Moreover a quantitative examination of the ELF data, beyond the visual analysis, corroborate the bonding picture offered by the topological bond orders based on ρ. Indeed, the fluctuations and the volumes of crucial ELF basins show that basins traditionally assigned as non-bonding should be viewed as having some bonding character, which increases the bond order from one to a value between one and two. Similarly, some traditionally assigned bonding density is in fact non-bonding, therefore reducing a "visual bond order" of two to less than two.

Comparison with previous work

The only previous work on this topic based on ELF is the recent work of Grützmacher and Fässler[41] Our work extends and amplifies their work, which was limited by the range of molecules studied, the level of the calculations, and the lack of quantitative data. Our more extensive study has led us to very different conclusions concerning the nature of the bonds in these molecules. In particular they restricted their study to H_2EEH_2 molecules using the extended Hückel model. In contrast we employ ab initio calculations and all-electron basis sets. Moreover, they did not attempt to distinguish between bonding (disynaptic) and non-bonding (monosynaptic) basins, or to obtain the basin populations, volumes and fluctuations by integration, which is an essential prerequisite to understanding bonding with the ELF method.

Based on their ELF plots Grützmacher and Fässler proposed the concept of the so-called slipped double or triple bonds, in line with a previous proposal by Klinkhammer and Schwarz.[12] They claim that the principal characteristic of a double bond is

the presence of the ELF maxima above and below the molecular plane, as found for the the C=C double bond in ethane. However, they hold on to this concept even if these maxima are moved considerably towards the E nuclei as they are for the heavier atoms. Consequently these authors designate the EE bonds (E = Si, Ge, Sn) as "slipped double bonds". Our study does not support this interpretation since we find that density moves out of the bonding region into the non-bonding region. Hence we find it unrealistic to insist that the main criterion for a double bond is that there is a maximum in ELF on either side of the internuclear axis irrespective of the position of these maxima. Accepting that it is more sensible to equate the bond order with the amount of bonding density the heavy element EE bonds become more like single bonds, which is consistent with the values of the AIM and ELF bond orders.

Equally, for supposedly triple bonds, the tilting of the central torus of six bonding electrons in REER implies that two of these electrons move closer to one atom core and two move closer to the other atom core leaving only two electrons in the unambiguous bonding region consistent with our interpretation that the bond order is less than three. The tilted torus can also be described in terms of a mixing in of a small contribution of the bottom right resonance structure into the bottom left resonance structure shown in Scheme 1. In our opinion the former makes a large contribution, which is consistent with the considerable length of the bond, compared to a classical "pure" triple bond. This is essentially confirmed by a study[42] on $[HGaGaH]^{2-}$ related to the present one.

A further remark concerns the ELF picture of planar Sn_2H_4,[41] which shows a disynaptic basin substantially extending towards the Sn nuclei, unlike the corresponding well-localized and central disynaptic basin in ethene. This important difference suggests that considerable non-bonding character is already present in the planar case and is hence not due to the trans bent equilibrium structure.

In summary we find that the designation of the EE bonds in REER and R_2EER_2 (E = Si, Ge, Sn; R = CH_3) systems as double and triple bonds is not in accord with the ELF analysis or with the widely accepted view that bond length is a useful criterion of bond order. We note that R_2SnSnR_2 molecules have very weak SnSn bonds that cause them to dissociate readily in solution to R_2Sn molecules, although Grützmacher and Fässler would describe the SnSn bond as a double bond.

Conclusions

In the series of REER and R_2EER_2 molecules (E = C, Si, Ge, and Sn) only the carbon molecules have what may be described as classical triple and double bonds. In all the other molecules it becomes increasingly difficult to describe the electrons as either bonding or non-bonding. Nevertheless it clear that through this series an increasing amount of the density has more non-bonding than bonding character and that the amount of bonding density decreases. It is the presence of this non-bonding density that is responsible for the non-linearity and non-planarity of the Si, Ge and Sn molecules. The increasing atomic size and decreasing electronegativity of the atoms in the series

C, Si, Ge and Sn has two important consequences: (1) the valence shell electrons are less attracted into the EE bonding region than in the carbon molecules so that the number of bonding electrons and hence the EE bond order decreases along the series. (2) The electrons are less localized into localized pairs than in the carbon molecules and it becomes increasingly difficult to distinguish between the bonding and non-bonding electrons. Although the number of bonding electrons (population of electrons in the bonding region) clearly decreases this decrease cannot be determined quantitatively, in other words no exact value can be given for the bond order. The most that can be said is that the EE bond order is less than three but greater than one in the REER molecules and decreases along the series, and that it is less than two and greater than one in the R_2EER_2 molecules and similarly decreases along the series. Indeed one must question if the concept of bond order has any quantitative significance for the Si, Ge, and Sn molecules. Nevertheless the ELF analysis shows that if the Si, Ge and Sn molecules are forced into the higher energy linear and planar conformations then some electron density is forced into the bonding region, increasing the "bond order" and decreasing the bond length correspondingly. But when this geometry relaxes to give the equilibrium geometry electron density moves from the bonding region to the non-bonding, even though these regions cannot be clearly defined. Classical Lewis structures are therefore inadequate for describing the bonding in these molecules. At best it can be approximately described in terms of the resonance structures shown in Scheme 1. In contrast to their carbon analogues we certainly cannot describe the bonds in the REER molecules (E = Si, Ge or Sn) as triple bonds or the bonds in the R_2EER_2 molecules as double bonds. They have fewer than six or four bonding electrons respectively with the remaining electrons playing the role of non-bonding electrons. Even to describe the non-bonding electrons as non-bonding pairs or lone pairs as is appropriate for the carbon molecules is a very rough approximation because the non-bonding electrons are not well localized into pairs.

Very briefly our main conclusions can be summarized as follows:

1. The EE bonds in the REER molecules (R = Si, Ge or Sn) have a bond order less than three but greater than one and the EE bonds in the R_2EER_2 molecules a bond order less than two but greater than one. These bond orders cannot be more precisely determined.

2. The electrons that are not attracted into the bonding region are present as non-bonding electrons and they cause these molecules to be non-linear and non-planar respectively.

3. The reason for the difference between the carbon molecules and those of the heavier elements is that the electrons are less localized and are less attracted into the bonding region in the molecules of the heavier elements because of the larger size and smaller electronegativities of the atoms of these elements.

Appendix

Topological analysis of the ELF function

Recognizing the major importance of the concept of localized groups of electrons Becke and Edgecombe introduced the electron localization function (ELF).[43] They claimed that theoretically meaningful definitions of electron localization must be sought in the density matrix itself and not in orbitals. The density matrix formulation of Hartree–Fock theory is suitable to define the conditional pair probability. This is the conditional probability of finding in space a given σ-spin electron if another electron with the same spin is located with certainty at a given position. The six-dimensional nature of this function is reduced to three-dimensions by calculating its spherical average. The leading term of a Taylor expansion of this spherically averaged

pair probability was shown[44] to contain D_σ, which is defined as

$$D_\sigma = \sum_i |\nabla \psi_i|^2 - \frac{1}{4} \frac{(\nabla \rho_\sigma)^2}{\rho_\sigma} \quad (1)$$

where ψ_i is a Hartree–Fock or Kohn–Sham spin orbital and the first term is a kinetic energy density. The truncated Taylor expansion demonstrates that the smaller D_σ, the smaller the probability of finding a second like-spin electron near the reference point. Alternatively D_σ represents the part of the local kinetic energy due to the Pauli principle.[45]

In the construction of ELF or $\eta(r)$ the function D_σ is divided by D_σ^0, which is the Thomas–Fermi kinetic energy density of the uniform electron gas, with spin-density equal to ρ_σ. Ensuring that ELF's upper limit of perfect localization corresponds to 1, we define,

$$\eta(\boldsymbol{r}) = \frac{1}{1 + \left(\dfrac{D_\sigma}{D_\sigma^0}\right)^2} \quad (2)$$

The upper limit of $\eta(r)$ is reached when the Pauli repulsion is weak, which happens when electrons are isolated or form pairs with antiparallel spins. The lower limit of $\eta(r)$ is zero and $\eta(r) = \frac{1}{2}$ corresponds to electron-gas-like pair probability.

Silvi and Savin were the first to apply[24] the topological analysis to ELF and show that the gradient vector field of ELF defines meaningful basins Ω, attractors and separatrices, just as in the electron density.[46,47] Volume integration over ELF basins yields interesting physical quantities, such as volume, population, fluctuation and relative fluctuation. If the integrand is the electron density one obtains the (average) population $N(\Omega_i)$. A measure of delocalization[48] is given by the quantum mechanical uncertainty on $N(\Omega_i)$, which is represented by its variance or fluctuation[49] $\sigma^2(N, \Omega_i)$, defined by

$$\sigma^2(N, \Omega_i) = \int_{\Omega_i} \mathrm{d}r_1 \int_{\Omega_i} \mathrm{d}r_2 \pi(r_1, r_2) + N(\Omega_i) - \left[N(\Omega_i)\right]^2 \quad (3)$$

where $\pi(r_1, r_2)$ is the spinless pair function.[50] Following Bader's definition[49] in the case of atomic basins (in ρ) the relative fluctuation is simply defined as

$$\lambda(N, \Omega_i) = \frac{\sigma^2(N, \Omega_i)}{N(\Omega_i)} \quad (4)$$

This quantity gauges the delocalization within a basin Ω_i. A value of 0.45 has been quoted before[25] as a sign of significant delocalization from a basin.

The contribution analysis[48] listed in Tables 2–7 shows the degree to which basins share their population. In order to obtain percentage contributions the elements of the cross exchange or covariance matrix[36] have been divided by the relevant basin populations. Only values higher than 10% have been quoted.

We supplement the topological information obtained from ELF with a bond order B_{AB} between two atoms A and B defined within the context of the topology of ρ rather than ELF. This bond order is calculated via eqn. (5),

$$B_{AB} = 2\sum_{ij} \{n_i^\alpha n_j^\alpha + n_i^\beta n_j^\beta\} < \phi_i | \phi_j >_A < \phi_j | \phi_i >_B \quad (5)$$

where n_i^σ is the occupation number of the ith spin-orbital $\psi_i(x)$ = $\phi_i(r)\sigma(s)$, $\phi_i(r)$ is a molecular orbital and $< \phi_i | \phi_j >_\Omega$ is an element of the atomic overlap matrix integrated over the basin of atom Ω. This equation was first proposed by Ángyán et al.[51]

who reformulated the "Mulliken–Mayer"[52] bond order. This bond order is defined as a partitioning in the Hilbert space spanned by the LCAO basis functions, similarly to the Mulliken population analysis, where the center of a basis function determines to which atom its contribution belongs. Ángyán *et al.* replaced this partitioning based on the center of the basis functions by the topological one, thereby introducing a bond order that is stable with respect to change in basis set (including the addition of diffuse functions). The bond order B_{AB} is similar to the delocalization index $\delta(A,B)$ proposed by Fradera *et al.*[53] The latter has also been defined within the context of the topology of ρ and becomes identical to B_{AB} for Hartree–Fock wave functions. For the purpose of the discussion in this paper the difference between the two topological bond orders is negligible.

Acknowledgements

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