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Recognizing a triple bond between main group atoms

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Abstract. The electron pair density, in conjunction with the theory of an atom in a molecule, enables one to unambiguously determine the nature of the bonding between the gallium atoms in bent $[HGa\text{-}GaH]^{2-}$. The Ga-Ga bonding in the dianion at the experimental bond length is found to be the result of the sharing of two electron pairs at the Hartree-Fock level of theory, the level consistent with the Lewis model of the electron pair.

Key words: *Ab initio* calculations – Bonding theory – Atoms in molecules theory (AIM) – Electron localization function (ELF)

1 Introduction

A paper recently appeared with the title "How can one recognize a triple bond between main group elements?" [1]. In this paper, Klinkhammer argues against the use of bond lengths and bond strengths in the answering of this question for the case of bonds between heavy electropositive atoms, while an appeal to theoretical calculations led to inconclusive statements. It is the purpose of this paper to point out that theory, in terms of the electron density, the pair density and the quantum theory of atoms defined as proper open systems, [2, 3] provides a unique and definitive answer to the question posed in the opening sentence. Proper open systems and their properties are defined by the quantum action principle and are identified with the atoms of chemistry because

(1) their properties are characteristic and additive, summing to yield the corresponding values for the molecule, and
(2) they are as transferable from one system to another as are the forms of the atoms in real space, that is, as transferable as are their charge distributions.

In particular, the atomic and group properties defined in this manner predict the experimentally determined contributions to the volume, energy, polarizability and magnetic susceptibility in those cases where the group contributions are essentially transferable, as well as additive.

The question posed by Klinkhammer [1] is of particular relevance for bonding between the heaviest elements of groups 13 to 16. Recent experimental work reported the synthesis of radical anions of the form $[R_2M\text{-}MR_2]^-$ with $M = Al$ or Ga, containing metal-metal bonds with a formal order of 3/2, and of $[R_3Ga_3]^{2-}$ with a formal order of 4/3 [4, 5]. Of particular interest to the present investigation is the compound $[RGa\text{-}GaR]^{2-}$ with R representing a bulky *m*-terphenyl substituent, recently synthesized by Robinson et al. as its disodium salt [6]. It represents the first molecule to formally possess a triple bond between heavy main group atoms. It is the modeling of the Ga-Ga interaction in this compound through the species $[HGa\text{-}GaH]^{2-}$ that was considered in the opening reference [1] and that is studied more thoroughly here, with the inclusion of the neutral species $Na_2[HGa\text{-}GaH]$. The works of Klinkhammer [1] and of others [7, 8] who considered the question of the multiplicity of the Ga-Ga interaction, use differing definitions of localized molecular orbitals in their interpretation and consequently reach different and uncertain conclusions to a problem that has a unique physical answer. More recently, Allen et al. [9] have presented an analysis of the bonding in the dianion that "rests primarily on the nature of the *canonical* molecular orbitals", providing as well, a comparison with and a critical assessment of the other orbital interpretations.

First, it is necessary to agree on a definition of multiple bonding, a concept that is inseparable from the Lewis model of the electron-pair bond. We accept

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This work is dedicated to the memory of Professor José Molina Molina, who passed away on 13th June 2000

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Klinkhammer's definition [1] when he states that 'a *covalent* bond consists of an electron pair which is *localized* on only two atoms, and a *triple* bond is defined by *three* covalent bonds connecting two atoms'. The quantum mechanical pair density in conjunction with the quantum definition of an atom in a molecule, provides a precise determination of the extent to which electrons are localized to a given atom or delocalized over any pair of atoms [10]. The pairing of electrons is a consequence of the Pauli exclusion principle and the spatial localization of the pairing is determined by the corresponding property of the density of the Fermi hole. The Fermi hole, the physical manifestation of the exclusion principle, has a simple physical interpretation: it provides a description of how the density of an electron of given spin, called the reference electron, is spread out from a preassigned point into the space of another, same-spin electron, thereby excluding the presence of an identical amount of same-spin density. It is a negative quantity, as it decreases the amount of same spin density throughout space. If the density of the Fermi hole is maximally localized in the vicinity of the reference point, then all other same-spin electrons are excluded from this vicinity and the reference electron is localized. For a closed-shell molecule, the result is a localized α,β pair. Correspondingly, the electron can go wherever its Fermi hole goes and if the Fermi hole of an electron, when referenced to a given atom, is delocalized into the basin of a second atom, then the electron is shared between them [10, 11].

2 Quantifying the spatial localization of electron pairs

The above ideas are made quantitative through the appropriate integration of the pair density to determine the total Fermi correlation contained within a single atomic basin, the quantity F(A,A), or the total correlation shared between two basins, the quantity F(A,B) [10, 12]. These quantities correspond to the corresponding double integration of the density of the Fermi hole weighted by the same spin density of the reference electron. At the Hartree-Fock level of theory, where the Fermi hole is the sole source of electron correlation, this procedure reduces an integration of the exchange portion of the pair density. F(A,B) then equals the number of same-spin electrons exchanged between the basins of the two atoms and F(A,A) equals the extent to which the N(A) electrons of atom A are exchanged within its own basin. The Hartree-Fock definition of F(A,B) is given in Eq. (1) in terms of $S_{ij}(A)$, the overlap of spin orbitals ϕ_i and ϕ_j over the basin of atom A:

$$F(A,B) = -\sum_i \sum_j S_{ij}(A) S_{ij}(B) \tag{1}$$

with a corresponding definition of F(B,A). The sums are performed once for the alpha spin orbitals and again for the beta spin orbitals to obtain the total number of electrons exchanged between the two atomic basins. F(A,B) measures the number of electrons of either spin referenced to atom A that are delocalized onto atom B. The sum F(A,B) + F(B,A) = δ(A,B) is termed the *delocalization index*. It is a measure of the total Fermi correlation shared between the atoms, that is, the number of shared electrons. Similarly, the quantity F(A,A) is given by

$$F(A,A) = -\sum_i \sum_j S_{ij}(A) S_{ij}(A) \tag{2}$$

Its limiting value is −N(A), corresponding to complete localization of the N(A) electrons to the basin of atom A [12]. The magnitude of F(A,A) is termed the *localization index* λ(A) and, in general, λ(A) < N(A), emphasizing that N(A) denotes an average population, the result of many electrons exchanging with the electrons in A and the average number of pairs in A is in excess of the limiting number 1/2 N(A)[N(A) − 1].

Just as the integration of the density of the Fermi hole over the space of the second electron yields minus one, corresponding to the removal of one same-spin charge, so the atomic and interatomic Fermi correlations sum to −N, the total number of electrons. Correspondingly, the localization and delocalization indices sum to N and they provide a quantitative measure of how the N electrons are localized within the atomic basins and delocalized between them [11, 12]. A corresponding relation holds for each atomic population N(A) where one has $N(A) = |F(A,A)| + \Sigma_{B\neq A}|F(A,B)|$ or, equivalently, $N(A) = \lambda(A) + \Sigma_{B\neq A}\ \delta(A,B)/2$. These expressions determine how the electron population of atom A is delocalized over the remaining atoms in the molecule.

Fulton [13a] and Angyan, Loos and Mayer [13b] have defined bond orders which, at the Hartree-Fock level of theory, yield values identical to those obtained using δ(A,B) but do so without reference to the underlying physics. That is, they do not relate their definitions to the properties of the density of the Fermi hole. Instead, Fulton uses products of terms in the first-order density matrix to describe the probability that one electron be found at two different points in space. Angyan et al. base their definition on the atomic partitioning of the exchange portion of the second-order Hartree-Fock density matrix, an expression whose form they choose to preserve even at correlated levels of theory to obtain what they term the "formal exchange component". Thus, with the inclusion of electron correlation the three methods give differing results and only δ(A,B) provides a measure of delocalization that is independent of any model and determined solely by the properties of the pair density. Since a non-vanishing delocalization index exists between every pair of atoms in a molecule, it is inappropriate to identify it with a bond order in the general case.

At the Hartree-Fock level the delocalization index equals unity for a single pair of electrons that is equally shared between two identical atoms A and A′. In this case, each electron contributes 1/4 to λ(A) and to λ(A′) and 1/2 to δ(A,A′). Thus, the Hartree-Fock description of H_2 yields λ(H) = λ(H′) = 1/2 and δ(H,H′) = 1.00. The electron pairing predicted by the Hartree-Fock model of the pair density is found to be remarkably successful in recovering the Lewis model [12]. For example, the Lewis model for N_2 requires δ(N,N′) = 3.00

for three shared electron pairs and $\lambda(\mathrm{N}) = \lambda(\mathrm{N}') = 5.50$, the latter being a result of a contribution of 1/2 from each shared pair and two from the 1*s* pair and two from the non-bonded pair of electrons that are assumed to be localized on each atom. The Hartree-Fock results are $\delta(\mathrm{N,N'}) = 3.04$ and $\lambda(\mathrm{N}) = 5.48$, indicating that the non-bonded density is delocalized to a slight degree. The delocalization values for the C-C atoms in ethane and ethylene at Hartree-Fock are 0.99 and 1.89, respectively. The delocalization indices for such homopolar interactions decrease with the addition of a Coulomb correlation, as it disrupts the pairing of electrons between the atoms. For example, with the addition of a Coulomb correlation, the value of $\delta(\mathrm{H,H'})$ decreases to 0.85 and $\delta(\mathrm{N,N'})$ to 2.2, while the values for $\delta(\mathrm{C,C'})$ decrease to 0.83 for ethane and to 1.42 for ethylene [12]. The values we report here are obtained at the Hartree-Fock level and they will thus represent upper limits to the number of Lewis electron pairs shared between equivalent atoms.

One can argue that comparisons of the Lewis model with the pairing of electrons determined by theory should be restricted to the single determinant (Hartree-Fock) model of the wave function. It is the Fermi correlation and only the Fermi correlation that determines the spatial pairing of electrons and this is the sole source of electron correlation at the Hartree-Fock level. In a real sense, the Hartree-Fock model retrieves the Lewis model from any, more general description of a molecular system.

Before proceeding with a discussion of the spatial pairing of the electrons found for the model of the Ga-Ga interaction, it is important to stress that only the pair density contains the information necessary for such a determination. The pair density is the expectation value of a quantum observable and as such, its value is independent of any unitary transformation used in its mode of representation. In particular, a unitary transformation of a set of orbitals leaves the pair density and its properties invariant [10]. Thus, the forms of canonical or localized orbitals, or of natural bond orbitals cannot be used to represent the spatial localization of electrons, a fact most easily appreciated by realizing that, in general, each choice of orbital representation will yield a different representation of the same physical event. The reader may, for example, compare the different representations of the three Ga-Ga "bonding orbitals" for $[\mathrm{HGa\text{-}GaH}]^{2-}$ obtained from an NBO analysis presented in one analysis [1] with the three localized molecular orbitals obtained in another [8]. Simply put, an electron is delocalized only if its Fermi hole is delocalized and the density of the Fermi hole remains unchanged whatever orbital set (obtained by a unitary transformation) one uses for its expression [10]. This simple but important observation invalidates the previous discussions.

3 Electron localization, the Laplacian of the density and ELF

The Laplacian of the electron density has been empirically related to the spatial localization of electron pairs because of its remarkable ability to faithfully mirror in terms of its local charge concentrations (CCs), the number, arrangement and relative sizes of the spatial domains associated with the bonded and non-bonded electron pairs whose presence is assumed in the VSEPR model of molecular geometry [2, 14]. Since a local charge concentration corresponds to a minimum in the Laplacian of the density, it is most convenient to discuss its topology in terms of the quantity $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$, a concentration of charge then corresponding to a maximum in $L(\mathbf{r})$. The geometrical patterns associated with differing numbers of electron pairs proposed in the VSEPR model [15] were based on the findings obtained by Lennard-Jones in his analysis of the properties of the same-spin pair density [16] and, consequently, one assumes the existence of some type of relation between the maxima exhibited by the topology of $L(\mathbf{r})$ and the pair density. It has recently been shown that this is indeed the case through the demonstration of a homeomorphism between the Laplacians of the electron density and of the conditional pair density obtained by a sampling of pair space by a reference pair of electrons [17]. The conditional pair density approaches the density in those regions of space removed from a localized pair of reference electrons. Under these conditions, the maxima in the negative of the Laplacian of the conditional pair density closely approximate the CCs of $L(\mathbf{r})$. This homeomorphism approaches an isomorphic mapping of one field onto the other, as the reference electron pair becomes increasingly localized to a given region of space. Thus, the CCs displayed in $L(\mathbf{r})$ signify the presence of spatial regions of partial pair condensation, regions with greater than average probabilities of occupation by a single pair of electrons and $L(\mathbf{r})$ provides a mapping of the essential aspects of electron pairing determined in six-dimensional space, onto the real space of the density.

The electron localization function (ELF) of Becke and Edgecombe [18] is empirically related to the conditional same-spin pair density and it is also used to locate the spatial regions of partial pair condensation [19]. In general, one observes a homeomorphism between the number and spatial arrangement of the maxima displayed by ELF and the CCs of $L(\mathbf{r})$ [11]. However, the maxima in ELF occur further removed from the relevant nucleus than those in $L(\mathbf{r})$ and, in the case of multiple bonding, the two fields can differ in the location and predicted number of maxima. Since $L(\mathbf{r})$ exhibits a homeomorphism with the Laplacian of the conditional same-spin pair density, it is the topology of $L(\mathbf{r})$ rather than that of ELF that is to be used in cases where the two fields differ in their predictions.

3 Previous calculations

Xie et al. [8] have reported extensive investigations of the local minima on the potential energy surfaces for $[\mathrm{HGa\text{-}GaH}]^{2-}$ and $\mathrm{Na_2[HGa\text{-}GaH]}$, as well as determining the optimized geometries for HGa-GaH and $\mathrm{H_2Ga\text{-}GaH_2}$. The latter two molecules formally possess double and single Ga-Ga bond orders, respectively. Xie et al. [8] find the global minimum for the dianion to be a doubly bridged butterfly geometry of C_{2v} symmetry that is approximately 9 kcal/mol in energy below that of the most stable open bent geometry that mimics that found in the crystal, the geometry that is predicted to be favored when H is replaced by large bulky groups as found in the crystal [20]. Two *trans* bent geometries of nearly equal energies are found, a planar one of C_{2h} symmetry and its twisted form with C_2 symmetry, the twisted form possessing a slightly lower energy, the energy difference decreasing with increasingly better calculations, equaling ~2 kcal/mol at Hartree-Fock and decreasing to 1 kcal/mol at MP2 using a 6-311++G** basis set, the set used in all of the calculations and one which closely duplicates the geometrical parameters obtained by Xie et al. [8]. The bent as opposed to the linear geometry in the case of the dimethyl derivative has been rationalized [21] in terms of a second-order Jahn-Teller distortion [22] resulting from the relatively small HOMO-LUMO gap found for the linear geometry. Of the various stable geometries found for $Na_2[HGa\text{-}GaH]$, only the symmetrical doubly bridged C_{2h} structure, analogous to that found in the crystal, is of relevance. The primary effect of the presence of the cations is to reduce the Ga-Ga separation; from 2.628 to 2.480 Å at the Hartree-Fock level. The Ga-Ga separation in the crystal is 2.319 Å, a value approached in an MP2 calculation that yields a separation of 2.470 Å for $[HGa\text{-}GaH]^{2-}$. The analysis of the number and pair density at the Hartree-Fock level is given for both the optimized C_{2h} geometry of $[HGa\text{-}GaH]^{2-}$ and for a C_{2h} geometry with the Ga-Ga separation fixed at the observed value of 2.319 Å with the remaining geometrical parameters re-optimized. Results are also reported for the stable *trans* bent C_{2h} geometry of HGa-GaH and for the twisted stable D_{2d} geometry of $H_2Ga\text{-}GaH_2$. The calculations are restricted to the Hartree-Fock level so as to enable a comparison of theory with the Lewis model and find that the principal features of the description of the bonding remain unaltered. In any event, Allen et al. [9] have performed a GVB correlated calculation for the dianion involving the orbital most likely to change in nature with the introduction of electron correlation, namely HOMO, and find that the principal features of the electron density remain unaltered.

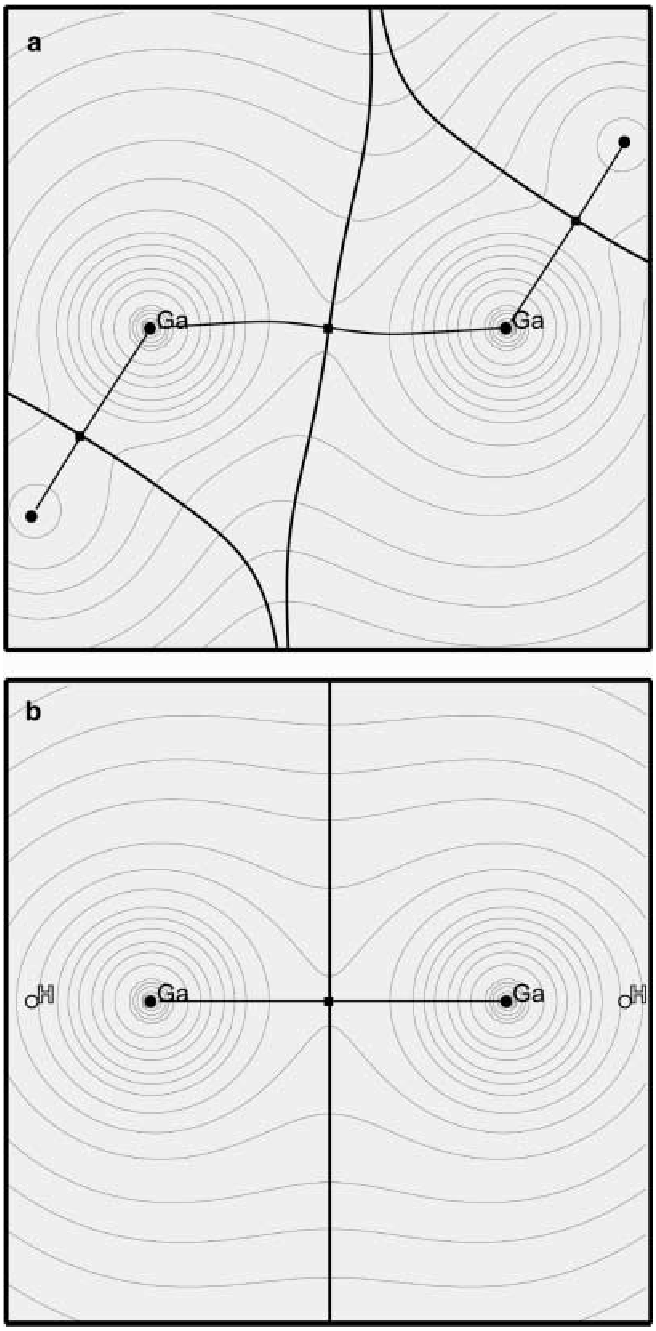

Fig. 1. Contour maps of the electron density distribution in $[HGa\text{-}GaH]^{2-}$ in the plane of the nuclei and in the perpendicular plane containing the Ga-Ga axis. The plots are overlaid with bond paths and atomic boundaries defined by the surfaces of zero-flux in the gradient vector field of the density. The contours increase in value inwards in steps of 2×10^n, 4×10^n and 8×10^n beginning with $n = -3$ and increasing in steps of unity. For b) the starting contour is 0.001 au. This distribution is distinguished from that for homopolar bonding between atoms from rows two and three by the relatively low value of the density in the region of the bond critical point

4 Computational methods

Ab initio HF/6-311++G** calculations were performed with the Gaussian 98 package of programs [23]. The AIM analysis has been done with the AIMPAC [24] series of programs, using the HF wave function as input as was described in the AIM theory [2]. The $\nabla^2\rho(r)$, and ELF contour-map representations have been produced using the MORPHY98 program [25].

5 Bonding between the gallium atoms

The Hartree-Fock electron density for two planes of the $[HGa\text{-}GaH]^{2-}$ molecule is displayed in Fig. 1. The plots are overlaid with the interatomic surfaces that define the atomic boundaries in these planes and the Ga-H and Ga-Ga bond paths that define the structure. Two atoms linked by a bond path are bonded to one another [26]. The atomic interactions are characterized by the density ρ_b, the Laplacian $\nabla^2\rho_b$ and the energy density H_b at the bond critical points, [2, 27] as given in Table 1 for the Ga-H interactions and in Table 2 for the Ga-Ga

Table 1. Critical point and delocalization data for H-Ga at the HF/6-311 + + G** theoretical level

Molecule	R(H-Ga) (Å)	q(H)	ρ_b (e/a_o^3)	$\nabla^2\rho_b$ (e/a_o^5)	H_b (Hartree/a_o^3)	δ(H,Ga)
$[Ga_2H_2]^{2-}$	1.617[a]	−0.62	0.102	+ 0.116	−0.051	0.87
$[Ga_2H_2]^{2-}$	1.640	−0.62	0.099	+ 0.105	−0.048	0.86
Ga_2H_2	1.628	−0.54	0.103	+ 0.104	−0.052	0.80
Ga_2H_4	1.582	−0.51	0.112	+ 0.136	−0.058	0.78

[a] The Ga-Ga distance fixed at the observed value of 2.319 Å with the remaining geometrical parameters re-optimized

Table 2. Critical point and delocalization data for Ga-Ga at the HF/6-311 + + G** theoretical level

Molecule	R(Ga-Ga) (Å)	q (Ga)	ρ_b (e/a_o^3)	$\nabla^2\rho_b$ (e/a_o^5)	H_b (Hartree/a_o^3)	δ (Ga,Ga)
$[Ga_2H_2]^{2-}$	2.319[a]	−0.38	0.067	+ 0.016	−0.029	2.02
$[Ga_2H_2]^{2-}$	2.628	−0.38	0.042	+ 0.075	−0.010	1.74
Ga_2H_2	2.788	+ 0.54	0.034	+ 0.009	−0.007	0.70
Ga_2H_4	2.532	+ 1.01	0.066	−0.043	−0.025	0.85

[a] The Ga-Ga distance fixed at the observed value of 2.319 Å with the remaining geometrical parameters re-optimized.

interactions. The entries are listed in the order of decreasing formal bond order. The data in Table 1 for Ga-H are indicative of a polar interaction, as is consistent with the values of q(H), the atomic charge [28] on H. The values of ρ_b are of the order 0.1 au, the values of $\nabla^2\rho_b > 0$ with all three curvatures of sizable magnitude, and $H_b < 0$. The negative energy density indicates that, unlike an interaction approaching the ionic limit, the potential energy density dominates over the kinetic energy density in the Ga-H interaction, a result of a significant sharing of density between the two atoms. This sharing is reflected in the delocalization indices that are of the order of 0.8. This does not imply a sharing of a corresponding fraction of a Lewis pair. Rather, it represents an unequal sharing of one pair in a polar interaction in the manner envisaged by Lewis who viewed the difference between the non-polar and polar extremes of bonding as corresponding to the equal or unequal sharing of the electron pair between two "kernels" [29].

The combination of values of the bond critical point parameters for the Ga-Ga interactions are non-typical of either the shared (covalent) or closed-shell extremes of interaction:

a) the value of ρ_b is surprisingly low for a homonuclear shared interaction, lying between 0.03 to 0.07 au, compared to values ranging from 0.14 au for B-B to 0.77 au for $N \equiv N$ interactions,
b) $\nabla^2\rho_b$ is close to zero, being slightly negative for the formal single bond, with the three individual contributing curvatures being of small magnitude in all cases,
c) the values for H_b are negative, ranging from −0.01 to −0.03 au.

The items a) and b) are associated with interactions approaching the closed-shell limit while c) is characteristic of a shared interaction. Such a mix of characteristics appears to be characteristic of metal-metal bonding [30]. The small values for H_b reflect the relatively small amount of valence density present in the internuclear regions of these molecules and the resulting small bond energies. Costales et al. [31] have investigated the bonding in nitride clusters containing group IIIB atoms using the topological indices. Included in this study is a listing of the bonding characteristics for N_2, Al_2, Ga_2 and In_2. They find values for ρ_b and $\nabla^2\rho_b$ for the Ga-Ga and In-In interactions similar to those reported here for the Ga-Ga interactions, with $\rho_b = 0.037$ au and $\nabla^2\rho_b = +0.008$ au for the gallium molecule, noting that the positive values of the Laplacian are a result of the absence of an outer valence shell of charge concentration in the gallium and indium atoms. Unlike behavior that is frequently found, the value of ρ_b does not exhibit a monotonic increase with a decrease in bond length and with an increase in formal bond order, as exhibited for example, by the C-C bonds in ethane, ethylene and acetylene [2]. Instead, the value of ρ_b for H_2Ga-GaH_2, which models a single bond, is equal to that for the dianion which models the triple bond at the experimental Ga-Ga separation, the shortest bond in Table 2. Anticipating the discussion of the delocalization indices, it is clear that one must distinguish between the value of the density in some region of space and the average number of electron pairs that contribute to that same region. An interaction with the largest value for ρ_b will not necessarily be the result of a sharing of the largest number of Lewis pairs. These observations echo those made by Klinkhammer [1] in a comparison of the interdependence of the bond length, bond strength and formal bond order exhibited by C-C bonds with the inapplicability of these same interdependencies for the present discussion. The lowest value of ρ_b is for HGa-GaH which formally models the double bond. As noted by Xie et al. [8] this molecule has an unusually long Ga-Ga separation. This bond and that in the dianion for the experimental separation are the only molecules in Table 2 to exhibit a significant ellipticity ε, the parameter that determines the preferred plane of charge accumulation in the case of an interaction that does not exhibit cylindrical symmetry in its density about the axis. The ellipticity of the Ga-Ga bond in HGa-GaH is 0.06 with the plane of accumulation coincident with the plane containing the nuclei, and not perpendicular to it as one might have anticipated in a model of a normal π bond. The ellipticity of the Ga-Ga interaction in the dianion is less than 0.01 for the optimized structure and increases to 0.08 au at the experimental separation, with the plane of the nuclei again being the preferred plane of charge accumulation. The disodium salt yields a conflict structure wherein the sodium atoms are linked by bond paths to the Ga-Ga bond critical point. The effect of this interaction is to create a marked ellipticity in the Ga-Ga interaction, equal to 0.53 with the diffuse density spread out in the plane containing the disodium axis and a modest increase of ρ_b to the value of 0.047 au.

The central question concerns the number of Lewis electron pairs that are shared between the two Ga atoms. The value of the delocalization index δ(Ga,Ga) for the dianion equals 1.7 for the Hartree-Fock optimized geometry and increases to 2.0 for the shorter experimental Ga-Ga separation (Table 2). Since the Hartree-Fock value represents an upper limit to the number of shared pairs of electrons, there is no Ga-Ga triple bond in $[Ga_2H_2]^{2-}$. The average number of electrons found within the basin of a gallium atom (its electron population) is 31.4. Of these, the pair density determines that 29.9 are localized on the atom, that is, $\lambda(Ga) = 29.9$, and the remaining electrons are delocalized onto and shared with the other atoms: 1.0 is shared with the second gallium atom, 0.4 with its bonded hydrogen and 0.1 with the second hydrogen. Similarly, for a hydrogen atom, $\lambda(H) = 1.1$ and of the average 1.6 electrons found within the basin of the hydrogen atom, 1.1 are localized on the atom. A further 0.4 are shared with the bonded gallium, 0.1 with the second gallium and 0.02 with the second hydrogen. Just under one Lewis pair is shared in the formal Ga-Ga single bond in $H_2Ga\text{-}GaH_2$. The large Ga-Ga separation in HGa-GaH which formally possesses a double bond, results in a low value of 0.7 for the delocalization index, as well as for ρ_b.

The prediction of a 'double bond' in terms of a direct count of the number of electron pairs shared between the two Ga atoms in the dianion at the experimental Ga-Ga separation is consistent with the topology exhibited by L(**r**), the Laplacian of the electron density, and by the electron localization function, ELF. The function L(**r**) exhibits three local maxima, three charge concentrations (CCs), in the outer shell of charge concentration of each Ga atom, Fig. 2. All CCs are in the plane of the nuclei, the largest with the value of 108 au is a bonding CC to H, the second largest with the value of 104 au, is a bonded CC to the second Ga and the third a non-bonded CC of the value of 103 au, is a non-bonded CC located on a line that forms an angle of 94° with the Ga-Ga axis. A single or a double bond is denoted in L(**r**) by the presence of a bonded CC in the VSCC of each of the participating atoms that can represent the presence of one or two shared pairs of electrons [11].

The CCs in gallium occur in the third quantum shell which, like the corresponding shell in the preceding transition metals, serves as the valence shell of charge concentration. Only from the elements arsenic onwards, does the number of quantum shells predicted by the Laplacian of either the electron density or the conditional pair density, exhibit a fourth shell of charge concentration. The number of maxima found in the outer shell of charge concentration of the transition metals up to germanium, does not in general correspond to the number of electron pairs anticipated on the basis of simple VSEPR models. Indeed, the VSEPR rules in general do not apply to transition metal molecules, which exhibit a unique pattern of CCs. The structure of the Laplacian of the density does however, provide a rationalization of the geometries of such molecules [32, 33]. In the present example, the three maxima in the VSCC of gallium do not represent the presence of three localized pairs of electrons, but rather regions of 'partial pair condensation'. These are regions where there is an increased probability of occupation by a single pair of electrons, but removed from the limit of localized pairs. The maxima associated with the bond paths connecting Ga to H and to the second Ga represent pairing associated with the bonding between these pairs of atoms, while from its location, the third CC is indicative of the presence of enhanced pairing in a non-bonded region. The outer shell of charge concentration in the Laplacian distribution of a Ga atom in the remaining two molecules also exhibits three CCs. In $H_2Ga\text{-}GaH_2$ two are bonding CCs to hydrogens and the remaining one is a bonding CC to the second Ga, a pattern consistent with the Lewis model if one associates a single bond with the bonded CCs shared between the gallium atoms. In HGa-GaH, one is a bonding CC to hydrogen, a non-bonded CC similarly located to

Fig. 2. Contour map for the Laplacian of the electron density in the region of a gallium atom in $[HGa\text{-}GaH]^{2-}$. The map illustrates the three local charge concentrations, CCs, (denoted by solid contours) in the outer shell of charge concentration of the gallium atom with values given in the text. These CCs denote the presence of regions of enhanced electron pairing associated with the bonding and non-bonding properties of the gallium atom density

that found in the dianion and the third is a bonding CC to the second Ga.

The corresponding hydrides of arsenic all exhibit Laplacian distributions that resemble those obtained for the second and third row elements: the VSCC containing the maxima in L(**r**) corresponds to the fourth quantum shell and the number and location of the maxima are as anticipated on the basis of the VSEPR model, exhibiting a pronounced bonded CC between the arsenic nuclei in each case. The value of δ(As,As) equals 3.0 in As_2, 1.97 in As_2H_2 and 0.99 in As_2H_4 [34].

ELF exhibits a pattern complementary to that found for the Laplacian of the density. There are two maxima in the plane of the nuclei in the neighborhood of each Ga corresponding to the bonded (to H) and the non-bonded maxima exhibited by the Laplacian (Fig. 3a). They bear the same angular relationship to one another as do the corresponding CCs in L(**r**) (Fig. 2). However, as is typical of the ELF representation of a double bond, two maxima are located midway between the Ga atoms, one on each side of the molecular plane, a pattern identical to that found for the double bond in ethylene [11, 35]. Klinkhammer [1] states in a footnote that ELF for the dianion "is in accordance with a triple bond within gallyne", a statement that is clearly incorrect. Thus, as with the Laplacian, one may not equate the number of maxima found in ELF with the formal count of the number of electron pairs, but rather as denoting the number of regions with enhanced degrees of electron pairing.

To demonstrate that the pattern of CCs in L(**r**) for each Ga atom in $[HGa\text{-}GaH]^{2-}$ are indeed a consequence of a partial condensation of the pair density, we have also determined the topology of the Laplacian of the conditional pair density for a fixed position of a reference pair of electrons. The local maxima in this function determine where one is most likely to find the remaining electron pairs when the reference pair is placed in a region of high localization, that is, a region where the Fermi hole is very localized. Placing the reference pair at the position of a Ga nucleus reproduces, in a near quantitative manner, the CCs of L(**r**) on the second Ga and those on the Ga whose nucleus serves as the reference point, to within better than one per cent. In particular, the CCs of L(**r**), their number and location, are faithfully reproduced in this display of the Laplacian of the conditional pair density demonstrating that the CCs of L(**r**) do indeed represent the number and locations of the sites of partial condensation of the pair density in real space.

Both Klinkhammer [1] and Xie et al. [8] conclude that the Ga-Ga bond is a triple bond. Xie et al. [8] ascribe the triple bond to the presence of a π bond and two weak dative bonds. The alternative picture obtained by Klinkhammer of a π bond, a σ bond and a 'slipped π bond' using NBOs is, according to Klinkhammer, equivalent to the description involving two dative bonds, since the two latter bonds are the orbital equivalents to the σ and slipped π bonds. Nonetheless, the slipped π bond has the appearance of being strongly localized in a non-bonded region of each gallium atom, reminiscent of the non-bonded CC in L(r), while the dative bonds point inwards and one is left with the troubling result that the two sets appear to provide different views of the Ga-Ga interaction. Along similar lines, using different orbital definitions of bond order, Wiberg's and the NBO scheme, Xie et al. [8] report values of 2.4 from the former and 3.0 from the latter. Allen et al. [9] focus their attention on the canonical HOMO of the dianion and criticize Klinkhammer's introduction of the 'slipped π

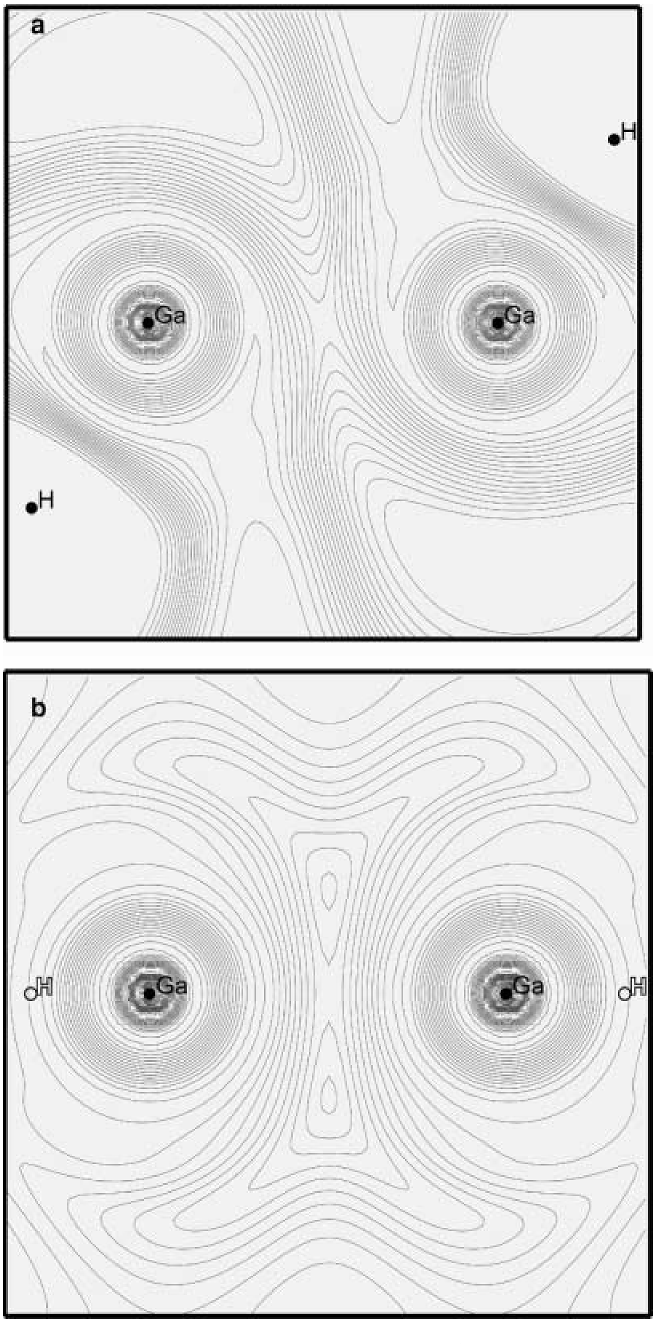

Fig. 3. Contour map of ELF for $[HGa\text{-}GaH]^{2-}$ for the same two planes shown in Fig. 1. The maxima in this function, which approach the value of unity, indicate that each gallium atom exhibits two regions of enhanced electron pairing: one associated with the bonding to hydrogen the other confined to a non-bonded region. In addition, there is a π-like pair of maxima situated midway between the gallium nuclei in the perpendicular plane

bond', claiming that it resembles the HOMO which they interpret as providing a description of the "lone pair density on the two gallium atoms in the regions geminal to the methyl groups." Thus, they argue that only two rather than three orbitals are involved with bonding, a point they further substantiate by performing a GVB calculation in which the HOMO was replaced by separated spin-pair orbitals, thereby maximizing the opportunity of obtaining a spin-pairing description of the associated pair of electrons. However, the resulting GVB orbitals are again concentrated away from the Ga-Ga internuclear region into the lone pair regions and correlation leaves the Hartree-Fock description unchanged.

The differing assignments given to the roles of the molecular orbitals in the attempts to employ them to determine the localization and spatial pairing of the electrons points to the difficulty with such approaches. The Laplacian of the density, in conjunction with the paralleling properties of the conditional pair density, provide clear and unequivocal answers to the number and role of the spatial regions of enhanced electron pairing. The pair density determines, again in an unequivocal manner, the number of electron pairs associated with the Ga-Ga interaction at the Hartree-Fock level of theory where the Lewis model is applicable.

The orbital descriptions are obtained by associating an electron pair bond with each of the three molecular orbitals that appear to be either shared between the two gallium atoms, as is the π bond, or semilocalized on each of the atoms, as are the dative bonds. One cannot equate the number of Lewis electron pairs associated with a given interatomic interaction to a corresponding number of 'participating' molecular orbitals, irrespective of whether or not the orbitals appear to be appropriately localized. This is most easily demonstrated by considering the expression for the quantity F(A,B) given in Eq. (1) in terms of the overlap of the spin orbitals over each of the atoms, that determines the total Fermi correlation shared between two atoms. This sum yields 3/2 for the N_2 molecule, and hence the delocalization index $\delta(A,B) = |F(A,B) + F(B,A)|$ equals 3. This is a result of each of the participating orbitals, one σ, one π_x and one π_y, being necessarily delocalized over just two atoms and each having a vanishing overlap with the others over each atomic basin. (Orbital orthogonality is a property associated with integration over all space.) The same is true for the C-C bond in acetylene except that there is some delocalization onto the hydrogen atoms and the index is decreased somewhat from the value three to 2.86. Orbitals, even localized orbitals, extend over all space and their properties do not in general reflect the degree of localization that is attributed to them, with the exception of core orbitals [10].

Loss of cylindrical symmetry in acetylene reducing the H-C-C bond angles to 120° to obtain a C_{2h} distortion corresponding to that found in $[HGa\text{-}GaH]^{2-}$, results in the creation of non-vanishing atomic overlaps of the σ orbitals with the in-plane π orbital that necessarily reduce the delocalization index, since $S_{\sigma\pi}(A) = -S_{\sigma\pi}(B)$ and the value is reduced to 2.64. These arguments remain true for whatever set of orbitals are used in the determination of the delocalization index. Thus, the value of $\delta(Ga,Ga)$ in the corresponding bent form of $[HGa\text{-}GaH]^{2-}$ is necessarily less than three because the loss of linear symmetry introduces an increased interference between the orbitals in the description of the pair density, an interference that is reflected in non-vanishing atomic overlaps that decrease the extent of delocalization. In addition, the 'bonding' orbitals are not completely localized on the gallium atoms, an effect that also reduces the number of pairs shared between the galliums. The statement by Xie et al. [8] that "Triple bonds do not require geometries to be linear." is incorrect when gauged in terms of the number of participating Lewis pairs determined by the pair density. Even they comment on the fact that there is much more mixing of the σ and in-plane π orbitals on bending $[HGa\text{-}GaH]^{2-}$ than occurs in bending HCCH and offer this as a reason for the greater associated decrease in the Wiberg bond index encountered in the former case.

Wiberg bond indices [36] are based on a Mulliken-type partitioning of the charge density-bond order matrix expressed in terms of contributions from atomic centered basis functions. Basis functions, like the molecular orbitals they are used to represent, extend over all space and blur the atomic identities. It is easily demonstrated that quantum mechanical expectation values are defined only for bounded regions of real space, a condition that includes, as a particular case, the total system bounded at infinity [37]. Therefore, if one wishes to use concepts defined in terms of quantum mechanical observables in the discussion of chemical bonding, then one is restricted to the use of atoms defined as proper open systems [3], an identification that is unique [38].

6 Conclusions

The Ga-Ga bond in bent $[HGa\text{-}GaH]^{2-}$ is a result of the sharing of two Lewis electron pairs, a double bond in the vernacular. This result is determined by a direct count of the number of electron pairs shared between the basins of the two gallium atoms using the Hartree-Fock pair density, the level of theory consistent with the Lewis electron pair model. It is in accord with the properties exhibited by the Laplacian of the density and by ELF, the topology of former function reflecting the spatial pairing of electrons as determined by the properties of the conditional pair density.

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