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The three-center-four-electron (3c-4e) bond nature revisited. An atoms-in-molecules theory (AIM) and ELF study

José Molina Molina, José A. Dobado

Grup de Modelització y Diseño Molecular, Instituto de Bioteccología, Campus Fuenteneuva s/n, Universidad de Granada, 18071-Granada, Spain, e-mail: dobado@ugr.es; Tel.: +34-958-243186; Fax: +34-958-243186

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Abstract. Theoretical calculations (B3LYP/6–311 + G**+) were performed on a series of formally hypervalent compounds showing linear three-center geometries. The bonding nature was analyzed by the electron density, $p(r)$, and electron-localization function (ELF) topologies, including calculations of the AIM charges and NMR chemical shifts (GIAO method). In addition, a quantitative analysis was also performed of the localization and delocalization indexes, obtained from the electron-pair density in conjunction with the definition of an atom in a molecule. Furthermore, the populations and fluctuations in the ELF basins were also evaluated. The compounds studied presented linear (1–5), T-shaped (6–9), and bipyramidal structures (10–15). Our results support the 3c-4e model for the linear (1–5) structures, but reveal for the T-shaped (6–9) structures only a small contribution from this model. In addition, there is no evidence to support the 3c-4e bond scheme for the bipyramidal compounds (10–15).

Key words: Ab initio calculations – Atoms-in-molecules – Bond theory – Three-center-four-electron bond – Electron localization function

1 Introduction

The bond nature in hypervalent compounds has long been controversial, and has been the object of several recent reviews [1, 2]. Special attention has been focused on chalcogen oxides [3] and ylides [4]. Historically, the bonding nature for these compounds has been based on an $sp^3d^3$ hybridization scheme. However, it is now clear from accurate ab initio calculations that $d$ orbitals do not participate in bonding, but act solely as polarization functions [1, 5]. The bonding schemes presented in the literature for hypervalent compounds arise from different analyses of the electronic wave function, indicating the importance of a rigorous and observation-based interpretation of the theoretical results [6]. The bonding properties of different linear, three-center hypervalent compounds have been characterized by the Rundle [7] and Pimentel [8] three-center-four-electron model (3c-4e). The application of this model to the $\text{[F}_3\text{]}^-$ molecule is depicted in Fig. 1.

A valence bond description of the 3c-4e scheme was performed by Linnett [9]. The 3c-4e model postulates three MOs, $\Psi_1$ with bonding nature, $\Psi_2$ with antibonding, and $\Psi_3$ with no bonding character. These three MOs yield an overall bond order of 0.5 with two electrons almost localized on the external fluorines with atomic charges of $-0.5\,\text{e}^-$. This scheme has also been extended to other hypervalent molecules such as $\text{F}_2\text{Cl}$, $\text{[F}_3\text{]}^-$, $\text{F}_4\text{S}$, $\text{F}_5\text{P}$, $\text{[F}_5\text{Si]}^-$ or $\text{F}_6\text{S}$, with different trigonal-bipyramidal or octahedral geometries. Furthermore, an explanation of the dissimilar ligand equatorial and axial bond lengths to the central atom is rationalized by these geometrical arrangements. Another point of view in the description of these hypervalent structures is the Generalized Valence Bond approach summarized by the democracy principle proposed by Cooper et al. [10], in which a particular atom uses any of its valence electrons in the chemical bonding, based on the principle of minimizing the total energy.

In recent years, an observation-based interpretative tool has been extensively used, the atoms-in-molecules (AIM) theory [11]. In this context, AIM has been used in the bonding description of different hypervalent compounds [3,4a,6,12]. A complementary method to study the chemical bonding is the electron-localization function (ELF) [13] analysis of Becke and Edgecombe [14]. Moreover, the ELF topological analysis has been also used to define chemical bonding including that in hypervalent molecules [12].

An appropriate definition of bonding indexes is of great importance for the bonding characterization of...
hypervalent compounds [15]. Therefore, much effort has been made in the past to define such a non-observable concept of chemical bonding [15, 16]. The corresponding covalent bond orders were defined both in the HF context or at the correlated level, while addressing the necessity of using the AIM atomic basins in the population analysis [16]. Moreover, other multi-center bond indexes have been proposed to study the 3c-4e model in the context of hypervalent molecules [17]. Considering that the bond is a non-observable concept in the Quantum Chemistry definition, electron-delocalization indexes have also been defined based on the pair density to link Quantum Mechanical and Classical approaches to chemical structures. This definition was made [18] using the Mulliken approximation to define charge density, bond order, etc., yielding indexes equivalent to those of Wiberg [19].

Another alternative is the delocalization indexes formulated by integration of the pair density between the atomic basins defined by the AIM theory [20, 21]. In this work, the 3c-4e bond model is revisited based on an adequate topological analysis of \( \rho(r) \) and ELF, together with the electron delocalization indexes proposed by Bader, and the theoretical NMR chemical shifts. The study has been performed for the hypervalent compounds depicted in Figs. 2 and 3. Geometrical and electronic calculations for 1–15 have already been extensively reported in the literature [22], including their \( \rho(r) \) and ELF analyses [12], and the results are compatible with the VSEPR model [23].

### 2 Computational details

#### General methods

Density functional theory (B3LYP) calculations were performed with the Gaussian 98 package of programs [24]. All the minimum structures were fully optimized and tested by frequency analysis at the B3LYP/6-311++G** level, yielding the minima with constrained symmetries (see Figs. 2 and 3) and non-imaginary frequencies. The AIM analysis [11] has been performed with the AIMPAC series of programs [25], using the DFT densities as the input.

The NMR chemical shifts were calculated by the GIAO [26] method using the tetramethylsilane (TMS) shielding as references for the \( ^1H \) (\( \delta_H \)) chemical shift (319.8 ppm).

The \( \nabla^2 \rho(r) \) contour-map representations have been produced using the MORPHY98 program [27]. The ELF analyses have been made with the ToPMoD package of programs [28].

#### Overview of the \( \rho(r) \) and ELF topologies

The topology of the electronic charge density, \( \rho(r) \), as pointed out by Bader [11], is an accurate mapping of the chemical concepts of atoms, bonds, and structures. The principal topological properties are summarized in terms of their critical points (CP) [11], and the nuclear positions behave topologically as local maxima in \( \rho(r) \). A bond critical point (BCP) is found between each pair of nuclei, which are considered to be linked by a chemical bond, with two negative curvatures, \( \varepsilon_1 \) and \( \varepsilon_2 \) and one positive \( \varepsilon_3 \) [denoted as \((3, -1)\) CP]. The ellipticity, \( \varepsilon \), of a bond is defined by means of the two negative curvatures in a BCP as:

\[
\varepsilon = \frac{\varepsilon_1}{\varepsilon_2} - 1, \quad \text{where} \quad |\varepsilon_2| < |\varepsilon_1|
\]  

(1)

The ring CPs are characterized by a single negative curvature. Each \((3, -1)\) CP generates a pair of gradient paths [11] which originate at a CP and terminate at neighboring attractors. This gradient path defines a line through the charge distribution linking the neighboring nuclei. Along this line, \( \rho(r) \) is a maximum with respect to any neighboring line. Such a line is referred to as an atomic interaction line [11]. The presence of an atomic-interaction line in such equilibrium geometry satisfies both the necessary and sufficient conditions that the atoms be bonded together.

The Laplacian of the electronic charge density, \( \nabla^2 \rho(r) \), describes two extreme situations. In the first, \( \rho(r) \) is locally concentrated \( |\nabla^2 \rho(r)| < 0 \) and in the second it is locally depleted \( |\nabla^2 \rho(r)| > 0 \). Thus, a value of \( \nabla^2 \rho(r) < 0 \) at a BCP is unambiguously related to a covalent bond, showing that a sharing of charge has taken place. In a closed-shell interaction, a value of \( \nabla^2 \rho(r) > 0 \) is expected, as found in noble gas repulsive states, ionic bonds, hydrogen bonds, and van der Waals molecules. Bader has also defined a local electronic energy density, \( E_d(r) \), as a function of the first-order density matrix:

\[
E_d(r) = G(r) + V(r)
\]  

(2)

where the \( G(r) \) and \( V(r) \) correspond to a local kinetic and potential energy density, respectively [11]. The sign of the \( E_d(r) \) determines whether a charge accumulation at a given point \( r \) is stabilizing \( E_d(r) < 0 \) or destabilizing \( E_d(r) > 0 \). Thus, a value of \( E_d(r) < 0 \) at a BCP presents a significant covalent contribution and, therefore, a lowering of the potential energy associated with the concentration of charge between the nuclei.

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 in a given atom and delocalized over any pair of atoms [21]. The electron pairing is a consequence of the Pauli exclusion principle, and the extent of spatial localization of the pairing is determined by the corresponding property of the Fermi hole density. These 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 \( F(A,B) \), the correlation shared between two basins. The quantity \( F(A,B) \) is thus a measure of the extent to which electrons of either spin referenced to atom A are delocalized into atom B with a corresponding definition of \( F(B,A) \). Thus, \( F(A,B) = F(A,B) \) and their sum, \( F(A,B) + F(B,A) = 2F(A,B) \), termed the delocalization index, is a measure of the total Fermi correlation shared between the atoms. This delocalization index is calculated taking into account that

\[
F(A,B) = F(B,A) = - \sum_i \sum_j S_i(A) \cdot S_j(B)
\]  

(3)

where \( S_j(A) \) is the corresponding atomic overlap matrix given by the PROAIM program at the Hartree-Fock level [20].

The ELF function [13, 14], which was first introduced by Becke and Edgecombe [14], can be viewed as a local measure of the Pauli repulsion between electrons due to the exclusion principle, enabling us to define regions of space that are associated with different electron pairs. The ELF function is expressed by

\[
\text{ELF} = \frac{1}{1 + \left( \frac{\rho}{\rho_c} \right)^2}
\]  

(4)