Theor Chem Account (2009) 122:51–66
DOI 10.1007/s00214-008-0484-x

REGULAR ARTICLE

The electronic structure of the F_2, Cl_2, Br_2 molecules: the description of charge-shift bonding within the generalized valence bond ansatz

André G. H. Barbosa · Alvaro M. Barcelos

Received: 12 August 2008 / Accepted: 19 September 2008 / Published online: 11 October 2008

Abstract In this paper, we present an alternative picture for the electronic structure of dihalogen molecules and for the physical origin of the "charge-shift bonding" effect. Absolute energies, binding energies, quadrupole moments and harmonic frequencies are determined for a hierarchy of methods from Hartree-Fock (HF), many forms of generalized valence bond (GVB) wavefunctions to Multi-Reference-MP2. All valence electron pairs are explicitly correlated in the GVB wavefunctions. It is shown that HF charge densities for the fluorine molecule are extremely inaccurate. This fact causes the HF canonical orbital basis for this molecule to be inadequate in low order correlation treatments in spite of the fact that there are no "near degeneracies" at the equilibrium distance. The accurate description charge fluctuation lone pair repulsions are essential for a proper assessment of the fluorine molecule binding energy, bond distance and harmonic frequency. These properties are well described by lifting the perfect-pairing restriction in a full-valence orbital optimized GVB-RCI (restricted-configuration-interaction) wavefunction. The accurate calculation of electron–electron cusps is of lesser importance in the description of the electronic structure of the fluorine molecule than usually considered. An analysis of the lone pair GVB natural orbitals provides a clear-cut understanding on the differences between fluorine and the other dihalogen molecules. Within our model, we conclude that among the dihalogen molecules the charge-shift bonding concept is meaningful only for the fluorine molecule.

Keywords Charge-shift bonding · Generalized valence bond · Fluorine · Chlorine · Bromine · Electronic correlation

1 Introduction

The chemical bonding in dihalogen molecules hides many interesting yet not fully understood specific features. The apparent discrepancy in the bond energies that should decrease as one moves down (F → I) in the periodic table is one of them [1]. In representative element groups, the homonuclear diatomic bonding dissociation energy decreases as one moves down in the periodic table. However, in the halogen group the chlorine molecule has the largest bond energy. The bond distance of the fluorine molecule is also considered to be a bit longer than expected for a first-row diatomic molecule. Additionally, the fluorine molecule is unbound at the Hartree-Fock (HF) level. Thus, dihalogen molecules, specially fluorine, are a stringent test for any ab initio approach attempting to describe their electronic structure and properties.

From a conceptual point of view, the bonding properties of molecules containing atoms bearing lone pairs have been successfully rationalized within the idea of "charge-shift" bonding. The reasoning and some calculation results that motivated the proposition of the charge-shift bonding mechanism are presented in the original paper of Hiberty et al. [2]. In order to validate the charge-shift bonding concept as a general mechanism for bonding it would be important to evaluate molecular model systems with complementary methodologies that allow for the emulation of this concept. By using a different methodology, we are able to bring additional understanding on the origin of this curious effect. In this paper,

---

A. G. H. Barbosa (✉) · A. M. Barcelos
Instituto de Química, Universidade Federal Fluminense,
Niterói, RJ 24020-141, Brazil
e-mail: andre@vm.uff.br

we propose an alternative way to understand the "charge-shift" effect on bonding using generalized valence bond (GVB)-like wavefunctions. In the process we will acquire additional insight on the physical mechanisms responsible for the binding in dihalogen molecules. Since the ground states of these molecules are all ${}^1\Sigma_g^+$ and none of them have the complications associated with "pi" bonding, they constitute a suitable set for the initial tests of the methodology.

2 Valence bond theory and charge-shift bonding

In classical valence bond theory the electronic wavefunction for a molecule is defined by an antisymmetrized spin-symmetry adapted superposition of products of atomic one-electron functions (atomic orbitals). Whether being hybridized or not, the orbitals are constrained to retain the form they have in the isolated atom. For lone pairs they are doubly occupied. With each spin-symmetry adapted product is associated a "chemical structure", i.e. a set of bonds and lone pairs that define a specific connectivity pattern between the atoms of the molecule [3, 4]. Most often in classical valence bond theory, the use of one "chemical structure" is insufficient to provide acceptable values for energies and molecular properties. The superposition (or "resonance") of "chemical structures", i.e. a non-orthogonal configuration interaction with more than one spin-symmetry adapted orbital product, usually brings quantitative accuracy to the method. However, for all but the smallest systems (up to few "active" electrons or electron-pair bonds) that accuracy is attained at a high computational cost limiting the size of the molecular system that can be treated.

The classical theory of valence [5] classifies the chemical bonds roughly in three types: covalent, ionic and polar covalent. These three kinds of interactions between two atoms (A and B) are represented through different weights associated with three possible resonance structures:

$A\bullet - \bullet B$ (covalent) A^+B^- and A^-B^+ (ionic)

A calculation based on the classical valence bond (VB) theory would consider the bond as covalent when the covalent structure has the lowest energy and the largest CI (configuration interaction) coefficient in the non-orthogonal superposition of the VB resonance structures. A bond would be considered ionic if one of the charge-separated structures has the lowest energy and the largest CI coefficient. In a polar covalent bond the covalent and one ionic structure would have roughly comparable energies and weights together perhaps with large resonance energy. Symbolically, for two-electron bond real wavefunctions, we would have:

$$\begin{aligned}
E &= \langle c_1\psi_{A-B} + c_2\psi_{A^+B^-} + c_3\psi_{A^-B^+}|H|c_1\psi_{A-B} \\
&\quad + c_2\psi_{A^+B^-} + c_3\psi_{A^-B^+}\rangle \\
E_{\text{covalent}} &\cong \langle\psi_{A-B}|H|\psi_{A-B}\rangle \\
E_{\text{ionic}} &\cong \langle\psi_{A^+B^-}|H|\psi_{A^+B^-}\rangle \\
E_{\text{covalent-polar}} &\cong c_1^2\langle\psi_{A-B}|H|\psi_{A-B}\rangle + c_2^2\langle\psi_{A^+B^-}|H|\psi_{A^+B^-}\rangle \\
&\quad + 2c_1c_2\langle\psi_{A-B}|H|\psi_{A^+B^-}\rangle \qquad (1)
\end{aligned}$$

In the expressions above B is more electronegative than A.

An improvement on the classical VB method was recently proposed by Hiberty et al. They call their method breathing-orbital-valence-bond (BOVB) [6–9]. The method is available in the Li and McWeeny's VB2000 code [10, 11]. It is unfortunate that the "BOVB" acronym is also used to name the bi-orthogonal-valence-bond method of McDouall [12–14]. In the present paper, the acronym "BOVB" would be used to refer only to the breathing-orbital-valence-bond method.

The BOVB wavefunction has the same general form of the classical VB function with one important difference. Although the orbitals are still purely atomic or hybridized in character, they are allowed to "breath", i.e. to shrink or swell, in order to minimize the total energy. Linear combinations with polarization functions within an atomic center are also allowed. In other words, the angular part of each orbital is still atomic centered while the radial factors are allowed to adjust in the optimization process. The atomic character of each active orbital is kept fixed in order to maintain the classical VB interpretation of the wavefunction. Since some orbital optimization is allowed, the BOVB expansion should be more compact than a corresponding VB expansion for a given molecule. Additionally, the superposition of different structures built with different orbitals leads to the inclusion of some amount of electronic correlation providing a fairly accurate wavefunction within a given basis set.

The chemical bond in the halogen molecules F_2, Cl_2 and Br_2 is traditionally considered to be a regular covalent bond. However, it has been suggested through BOVB calculations that the covalent bond in many molecules containing electronegative first-row elements with lone pairs is fundamentally different from a regular covalent bond. They identify the special character found in these systems under the name of "charge-shift" bonding [2, 15–17]. In BOVB calculations, qualitatively correct bond dissociation energies (BDE) for these systems can only be attained with a superposition of three terms:

$$\begin{aligned}
E_{\text{charge-shift}} &\cong c_1^2\langle\psi_{A-B}|H|\psi_{A-B}\rangle + 2c_1c_2\langle\psi_{A-B}|H|\psi_{A^+B^-}\rangle \\
&\quad + 2c_1c_3\langle\psi_{A-B}|H|\psi_{A^-B^+}\rangle \qquad (2)
\end{aligned}$$

The distinct feature of the "charge-shift bonding" is that the "resonance" terms (the cross terms in the expression above) are the only ones responsible for bonding, the covalent structure bringing little or none energetic stabilization to the associated wavefunction. Bonds between electronegative atoms bearing valence lone electron pairs should be particularly prone to exhibit charge-shift bonding. We believe that this apparently counterintuitive effect remained uncovered for many years for three reasons. First, the cross terms in the expression above were assumed to be unimportant for the description of bonding, and consequently they were almost never explicitly calculated. Second, due to limitations in computer power, a necessary working hypothesis for many practitioners in VB theory was to ignore the influence of lone pairs and to approximately consider that all important effects were contained in the bonding electron pairs. Third, lone pairs are much more difficult to split in singly occupied orbitals and their explicit description necessarily demands extensive basis sets. The BOVB method manages to treat lone pairs because it relies on a superposition of different structures with different orbitals. This superposition allows the description of the variations of the charge density associated with the charge-shift bonding effect. Hence, it seems that it would be necessary to use a multistructure VB method to calculate properties of charge-shift bonded molecules. Because of that, the authors claim that the GVB wave function [18] would be unable to describe in a qualitatively correct way charge-shift bonded systems [8]. They support this claim with the fact that the BDE of the fluorine molecule calculated with a GVB(1/2)-perfect-pairing-(PP) wave function is less than half of the experimental value (see Table 1). Since the charge-shift effect is in part associated with the existence of lone pairs in the bonding atoms, we believe that the GVB approach cannot be ruled out based on calculations which did not explicitly include lone pairs. The question is: how could one emulate the charge-shift effect with a GVB-like wavefunction? In this paper, we will provide a possible answer for this question. In doing so, we will present an alternative physical picture to understand the charge-shift bonding effect. GVB wavefunctions do not allow a clear-cut interpretation in terms of covalent–ionic resonance. On the other hand they are uniquely defined in the variational sense, they always satisfy the virial theorem and yield more compact wavefunctions than atomic-orbital-based VB methods. Hence, our approach for analyzing and interpreting the results will be necessarily different than the ones used in the original proposition of the charge-shift bonding concept. Thanks to specific features of different kinds of GVB and MCSCF wavefunctions, we will be able to identify in the wavefunction the influence of left–right correlation, lone pair repulsion, charge transfer and dynamic correlation (Coulomb hole) effects. That will improve our understanding on the physical origin of the charge-shift bonding effect in the fluorine molecule. In order to present a self-contained argumentation, and to justify the present approach, in the first place we should briefly review some of the fundamental features of GVB-like wavefunctions.

Table 1 Absolute energies (a.u.) for optimized equilibrium geometries and dissociated atoms, bond dissociation energy (kcal/mol), optimized bond distance (Å) and harmonic vibrational frequency (cm^{-1}) for the F_2 molecule at different levels of calculation

	E_{req}	E_{diss}	D_e	r_{eq}	v
HF	−198.760936	−198.804166	−27.1	1.328	1,260
GVB(1/2)-PP	−198.830605	−198.804166	16.6	1.467	703
GVB(7/14)-PP	−198.884799	−198.856913	17.5	1.472	780
GVB(7/21)-PP	−198.893478	−198.869119	15.3	1.471	697
GVB-RCI(7/14)	−198.999487	−198.947640	32.5	1.415	900
CASSCF(14,14)	−199.016938	−198.952763	40.3	1.406	956
MP2-frozen core	−199.290907	−199.236408	34.2	1.401	995
(2,2)MR-MP2	−199.294672	−199.236408	36.6	1.428	888
Experimental [1]			38.2	1.412	917

All calculations performed with the aug-cc-pVTZ basis set

3 Generalized valence bond wavefunctions and charge-shift bonding

In this work, we propose an alternative way to express charge-shift bonding effects in dihalogen molecules using GVB-like wavefunctions as reference. Due to the general misunderstandings found in the literature concerning modern VB approaches, it is appropriate to recall the rationale behind the GVB ansatz in order to better appreciate our model for charge-shift bonding.

In 1926, studying the He atom, Heisenberg recognized that coordinate permutations among different electrons in a two-electron system were a constant of motion of the many-particle Hamiltonian [19, 20]. Soon after, Wigner generalized this notion in a more precise way stating that since electrons were indistinguishable in many electron systems, an electronic wavefunction must correspond to a representation of the permutation group [21]. In the following year, it appeared in the work of Heitler and London on the H_2 homopolar bond, which became the prototype of the classical VB approach to electronic structure [22]. The covalent bond energy was properly accounted for the first time through a two-term wavefunction conforming to the previous ideas of Heisenberg and Wigner:

$$\Psi_{\mathrm{HL}}(H_2) = \frac{1}{\sqrt{2}}[1s_{\mathrm{a}}1s_{\mathrm{b}} + 1s_{\mathrm{b}}1s_{\mathrm{a}}] \tag{3}$$

Both electrons were allowed to occupy $1s$ atomic orbitals centered in "a" and "b" nuclei. This wavefunction corresponds to a faithful representation for the permutation group of electron coordinates as established by Wigner. In 1949, Coulson and Fischer [23] showed that an approximate orbital optimization procedure applied on the Heitler and London wavefunction caused one important effect. The fully optimized orbitals lose their pure atomic character by delocalizing towards the other atom to which it is making a bond. By doing that, the system experiences an energy lowering that the authors associated with the ionic–covalent superposition of classical VB theory. Note that this association is only valid if one ignores the Hamiltonian cross matrix elements between different "chemical structures". In late 1960s, Goddard [24–28] and Gerratt [29] working independently took up the problem of generating wavefunctions that correspond to faithful representations of the permutation group incorporating orbital optimization from the outset. In order to emphasize the group theoretical significance of their propositions they name their approaches as GI and spin-coupled (SC). Since the group theoretical machinery used was not common knowledge among the chemistry community (as still not is today), they soon have attempted to present their methods as generalizations of the classical VB ansatz in the sense of Coulson and Fisher. The name GI was replaced by GVB [18] and SC wavefunctions began to be frequently referred as a "Modern VB" approach [30]. There are almost as many "generalizations" of the Heitler and London approach as there are researchers in the "VB field". Nevertheless, the fact remains that contrary to most of the literature in the area, in these two approaches a complete treatment of both permutation degeneracy and orbital optimization is simultaneously attempted. Besides that, in the last 40 years the majority of papers published in the literature applying a VB-like method to chemical systems have employed GVB or SC wavefunctions [31–33]. For these reasons, if the charge-shift bonding concept is to be incorporated to the conceptual framework of quantum chemistry it should have an expression using GVB or SC wavefunctions.

The GVB methodology is usually applied in its most restricted form called strong-orthogonal-generalized-valence-bond-perfect-pairing-($N/2N$), where N pairs of electrons are described with $2N$ singly occupied orbitals [18, 34]. Separating the core electrons and considering N valence pairs of orbitals the unormalized SO-GVB-PP wavefunction can be written as the antisymmetrized product:

$$\Psi_{\mathrm{GVB-PP}} = \mathrm{A}\left|\mathrm{core}\left[\prod_{\substack{k=1\\ i=2k-1\\ j=2k}}^{N}\left(\psi_i\psi_j + \psi_j\psi_i\right)_k \alpha\beta\right]\right\| \tag{4}$$

The singly occupied orbitals allocated in different pairs are strongly orthogonal [35] and the two orbitals within a pair are free to overlap. Note also that regardless of the number of electrons, there is only one form of spin coupling considered for a given S^2 and S_z values. In this restricted form, the SO-GVB-PP wavefunction is a particular case of the antisymmetrized product of strong-orthogonal geminals (APSG) wavefunction of Hurley et al. [36, 37] where there is no restriction on the number of orbitals that describe an electron pair. Applications of the SO-GVB-PP wavefunction were fostered mainly by three particular features. Firstly, from the computational point of view the expansion above can be rewritten as a multi-configuration-self-consistent-field (MCSCF) expansion with doubly occupied orthogonal orbitals [34, 38]:

$$\Psi_{\mathrm{GVB-PP}} = \mathrm{A}\left|\mathrm{core}\left[\prod_{\substack{k=1\\ i=2k-1\\ j=2k}}^{N}\left(c_{ii}\varphi_{ii} + c_{jj}\varphi_{jj}\right)_k \alpha\beta\right]\right\| \tag{5}$$

In the MCSCF form, the SO-GVB-PP orbitals within each pair assume the appealing shape of bonding/antibonding localized natural molecular orbitals. In this form, the wavefunction can be efficiently calculated with a Fock-operator-based approach also suitable for completely general HF-open-shell configurations. Secondly, in this approximation the SO-GVB-PP wavefunction still constitute an independent-particle-model (IPM) allowing a well-defined physical interpretation of the singly occupied non-orthogonal orbitals. Thirdly, it is able to correctly describe singlet diradicals and dissociation products from the breaking of single bonds. On the other hand, the SO-GVB-PP wavefunction still lacks dynamic correlation and it is not able to describe systems where more than one form of spin coupling have large coefficient. Typical situations where the SO-GVB-PP is unable to provide qualitatively correct pictures are the dissociation of multiple bonds and the electronic structure of aromatic systems.

The highest level of calculation that should not describe the effects associated with charge-shift bonding is the SO-GVB-PP level with the same number of electrons and orbitals in the "active" space. At this level we include left–right correlation within each bonding pair. We also improve the description of lone pairs by splitting them in two singly occupied non-orthogonal orbitals. Both effects are associated with the proper treatment of the permutation degeneracy within a given electron pair. Each active space electron pair is described by two orthogonal orbitals that are strongly orthogonal to all the other orbitals. This approximation provides an unambiguous way to approach the so-called "Pauli repulsion" among different electron pairs. The origin of this effect lies on the permutation and spin degeneracy of the electron coordinates and is fully discussed elsewhere [4, 24–29, 39, 40]. In the simple SO-GVB-PP approximation, the electron pairs are described by uniquely defined variationally optimized orbital pairs. Hence, we have an unique correspondence between electron pairs and localized orbital pairs. "Pauli repulsions" have the effect to prevent the spatial interpenetration of charge densities associated with different electron pairs. The practical consequence is to limit the interaction among different electron pairs to Coulomb repulsion. Any overlap or interference effect is avoided. This restriction can only be relaxed by extensive configuration interaction or, equivalently, by considering other spin functions and non-orthogonal orbitals. Since in all GVB wavefunctions used in this paper the electron pairs are described by an unique set of orthogonal natural orbitals, for the moment we will refrain from using the term "Pauli repulsion" and use only the simpler and less obscure "lone pair repulsion". Some other important physical effects such as interpair correlations, charge transfer and dynamic correlation (Coulomb hole) effects are absent from the GVB-PP wavefunction. Hence, we do not expect to describe charge-shift bonding effects at this calculation level. For this reason, the SO-GVB-PP level is our reference for the evaluation of the importance of these additional effects in the bonding of dihalogen molecules.

One way to improve the SO-GVB-PP wavefunction is to consider other spin functions in addition to the "perfect-pairing" one. If extra spin functions are considered with the wavefunction retaining the feature of being described by sets of variationally optimized bonding and antibonding pairs of orthogonal orbitals we would have the so-called SO-GVB [38, 41–43] wavefunction. Within each pair, an additional open-shell spatial configuration with each the bonding and the antibonding orbital being singly occupied is allowed. In this open-shell configuration, the electron pair may be coupled in singlet or triplet. In true SO-GVB calculations the open-shell singlet coupling in each pair is transformed away into an intrapair orbital rotation, being eliminated from the total wavefunction [43]. The possible interaction between singlet open-shell configurations in different pairs is taken out of the Hamiltonian. The singly occupied non-orthogonal orbitals of the SOGVB wavefunction still support an independent particle approximation. If one retains all intrapair open-shell singlet coupled configurations we have the GVB-RCI (restricted-configuration-interaction) [38, 44, 45]. The GVB-RCI wavefunction have been much more used than the SO-GVB ansatz in spite of the fact that it is no longer an independent particle model. In the present paper, we have always used the GVB-RCI wavefunction with variationally optimized orbitals. For an even number of active electrons, the GVB-RCI wavefunction for N valence pairs may be written as:

$$\Psi_{\mathrm{GVB-RCI}} = \mathrm{A}\left|\mathrm{core}\left[\prod_{\substack{k=1\\ i=2k-1\\ j=2k}}^{N}\left(c_{ii}^{k}\varphi_{ii}+c_{jj}^{k}\varphi_{jj}+c_{ij}^{k}\varphi_{i}\varphi_{j}+c_{ji}^{k}\varphi_{j}\varphi_{i}\right)\left[c_{k}\alpha\beta+c_{k}^{*}(\alpha\alpha\pm\beta\beta)\right]\right]\right| \qquad (6)$$

All possible open-shell configurations that keep two electrons in each bonding/antibonding pair are incorporated in the CI expansion. In VB terms, it means that all possible spin functions for that number of electrons with a given total spin are included in the wavefunction. It is very important to note that the GVB-RCI wavefunction is still fundamentally different from the SC or unrestricted GVB ansatz. In the GVB-RCI wavefunction, the orbitals are fully optimal only for one (perfect-pairing) spin coupling. In the SC or unrestricted GVB wavefunctions the optimal orbitals have no orthogonality restrictions whatsoever and are determined in relation to a variationally optimized average of all possible spin couplings compatible with given S^2 and S_z values. When the system is dominated by one form of spin coupling, the wavefunction obtained with GVB-RCI ansatz should be lower in energy than the one obtained with the SC approach. On the other hand, when more than one spin coupling is qualitatively important the electronic energies obtained with the SC wavefunction should either be the same or lower than the ones obtained with the GVB-RCI wavefunction [46].

In terms more often used for correlation energy analysis, we could say that the major difference between the SO-GVB-PP and the GVB-RCI wavefunction is the incorporation of disconnected clusters of single excitations. As shown by Van Voorhis and Head-Gordon [47], the configurations associated with the linear expansion of the GVB-RCI wavefunction can be formally generated by an orbital restricted exponential cluster operator. Thus, as the GVB-PP wavefunction can be viewed as an orbital constrained variational form of coupled-cluster-doubles (CCD) [48], the GVB-RCI wavefunction can be viewed as an orbital constrained variational form of coupled-cluster-singles-and-doubles (CCSD). In the converged GVB-RCI linear expansion for closed-shell systems with variationally optimized orbitals the open-shell excited configurations are all of even order (doubles, quadruples, sextuples, etc.). Note that the energy associated with a GVB-RCI wavefunction is always higher than the energy obtained with a complete-active-self-consistent-field (CASSCF) [49] wavefunction defined in the same number of electrons and orbitals. Any energy lowering caused by the inclusion of these open-shell configurations used in the GVB-RCI do not correspond to dynamic correlation energy (in the Coulomb hole sense) since they are all disconnected clusters of singles. A single excitation describes the wavefunction relaxation. It can be rephrased as an orbital rotation between occupied and virtual spaces. This fact forms the basis of variational optimization procedures of MCSCF wavefunctions [50, 51] through the Generalized Brillouin Theorem [52]. Even order disconnected clusters of single excitations account for simultaneous electronic polarization in different regions of an atom or molecule [4].

The GVB-RCI includes all the spin couplings compatible for a given "S^2" and "S_z" values without allowing net electron donation between different bonds and lone pairs. The main difference between a CASSCF and a GVB-RCI defined in the same number of orbitals and with the same number of electrons is the presence of all possible charge transfer configurations. In the GVB-RCI expansion each bonding/antibonding pair is always occupied by two electrons. In the CASSCF expansion the same bonding/antibonding pair can be occupied from zero up to four electrons. If we employ the same localized natural orbital basis the additional configurations can be associated with the charge transfer within an atom or among different atoms. In order to evaluate the influence of charge transfer effects between the halogen atoms, we can define an arbitrary intermediate wavefunction that lie halfway GVB-RCI and CASSCF. All unique optimized natural orbitals are localized at the GVB-RCI level. We can associate one orbital pair with the chemical bond. Hence, each one of the other six orbital pairs is necessarily associated with one of the halogen atoms valence lone pairs. Defining a constrained CASSCF wavefunction that allows charge transfer only within an atom would provide a fair reference to evaluate the importance of interatomic charge transfer effects. Thus, our choice for reference function to evaluate charge transfer effects is the constrained-CASSCF wavefunction defined in the localized GVB-RCI natural orbitals. The effect of interatomic charge transfer in the total energy will be evaluated as the difference between the constrained-CASSCF and the CASSCF wavefunctions. Note that if we kept ourselves to CASSCF(N,N) wavefunctions we will not include dynamic correlation (Coulomb hole) effects. True dynamic correlation effects can only be described by a CASSCF wavefunction when one has a larger number of active orbitals than the number of active electrons [49, 53]. We will show that by including all possible open-shell configurations in the GVB-RCI wave function, we can obtain a reasonable description of the bonding in the fluorine molecule without explicitly considering the charge transfer configurations among the fluorine atoms. On the other hand, for the chlorine and bromine molecules, the importance of charge transfer configurations is shown to be significantly larger. These findings will demonstrate that the GVB wavefunction ansatz can indeed accommodate most of the effects responsible for binding in these molecules, bringing new insights on their electronic structure.

4 Computational details

We have performed ab initio calculations and BDE evaluations at the HF, SO-GVB(1/2)-PP, SO-GVB(7/14)-PP, SO-GVB(7/21)-PP, SO-GVB-RCI(7/14), CASSCF(14,14), MP2(valence) and (2,2)MR-MP2 [54] levels. Electric quadrupole calculations were performed for all these levels but (2,2)MR-MP2. Harmonic vibrational frequencies were also calculated. Since all GVB wavefunctions were built with strong-orthogonal orbitals we will drop the prefix "SO" on their designations. The standard aug-cc-pVTZ basis set was used for all atoms in all calculations. The basis set used is large enough such that qualitative errors in the properties calculated here should not be attributed to its limited size.

All GVB wavefunctions were emulated as multiconfiguration-self-consistent-field (MCSCF) calculations in the GAMESS [55] code using orthogonal orbitals. The core orbitals were fully optimized within the doubly occupation restriction as usually done in MCSCF calculations. The GVB-RCI wavefunctions were calculated with Ivanic's occupation-restricted-multiple-active-space (ORMAS) code as implemented in the GAMESS package [56, 57]. The configurations that define the different GVB-PP wavefunctions were taken from a spatial configuration generation code written by one of us (AGHB).

The starting orbitals for the GVB calculations were taken from localized occupied and virtual HF orbitals. The valence canonical molecular orbital configuration of the three dihalogen molecules can be pictured as:

$$[\mathrm{core}]1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4$$

The canonical molecular orbitals obtained in a HF-MO calculation were localized using the Pipek-Mezey

Table 2 Quadrupole moment (in Buckinghams) for fluorine, chlorine and bromine molecules at different levels of calculation

	F_2			Cl_2			Br_2		
	XX	*YY*	*ZZ*	*XX*	*YY*	*ZZ*	*XX*	*YY*	*ZZ*
HF	−0.24	−0.24	+0.48	−1.55	−1.55	+3.10	−2.28	−2.28	+4.56
GVB(1/2)-PP	−0.54	−0.54	+1.08	−1.72	−1.72	+3.44	−2.47	−2.47	+4.94
GVB(7/14)-PP (2*s*,4*p*)	−0.56	−0.56	+1.12	−1.61	−1.61	+3.22	−2.36	−2.36	+4.72
GVB(7/21)-PP (2*s*, 4*p*)	−0.55	−0.55	+1.10	−1.58	−1.58	+3.16	−2.35	−2.35	+4.70
GVB-RCI(7/14)	−0.50	−0.50	+1.00	−1.67	−1.67	+3.34	−2.55	−2.55	+5.10
CASSCF(14,14)	−0.50	−0.50	+1.00	−1.57	−1.57	+3.14	−2.23	−2.23	+4.46
MP2 (frozen core)	−0.51	−0.51	+1.02	−1.64	−1.64	+3.28	−2.40	−2.40	+4.80

The molecules lie along the *Z* axis

algorithm [58]. The resulting localized orthogonal orbitals constitute the following electronic configuration admitting two atoms “A” and “B”:

$$[\text{core}]s_{\text{A}}^2 s_{\text{B}}^2 \sigma_{\text{AB}}^2 p_{x\text{A}}^2 p_{y\text{A}}^2 p_{x\text{B}}^2 p_{y\text{B}}^2$$

The names *s* and *p* do not mean that these are true atomic orbitals but just “*s*-like” and “*p*-like” molecular orbitals localized mainly on one of the atoms. The virtual space was treated in the same way in order to generate orbitals localized in the same region of the ones in the occupied space. The GVB pairs were formed by pairing one occupied and one (two) virtual(s) orbital(s) localized in the same region of space.

$$[\text{core}]\left(s_{\text{A}}s_{\text{A}}^*\right)^2\left(s_{\text{B}}s_{\text{B}}^*\right)^2\left(\sigma_{\text{AB}}\sigma_{\text{AB}}^*\right)^2\left(p_{x\text{A}}p_{x\text{A}}^*\right)^2\left(p_{x\text{B}}p_{x\text{B}}^*\right)^2 \times \left(p_{y\text{A}}p_{y\text{A}}^*\right)^2\left(p_{y\text{B}}p_{y\text{B}}^*\right)^2$$

The binding energy at each level was taken as the difference between the energy associated with the optimized molecular geometry and the energy at infinite distance. The separated fragment energies were calculated in two ways [59]. In the supermolecule approach, we calculated the energy associated with a very large bond distance between the halogen atoms. In the other approach, we determine the dissociated reference as twice the energy of one isolated halogen atom in the presence of the basis functions of the other atom. Both approaches led to identical results. For the wavefunctions that were not size-consistent in open-shell fragmentation, i.e. HF and MP2, the GVB(1/2)-PP and (2,2)MR-MP2 were, respectively, used as dissociated reference.

5 Results and discussion

5.1 Fluorine

The bond dissociation energies (BDE), bond distances optimized at each level of calculation and harmonic vibrational frequencies for the fluorine molecule are presented in Table 1.

As is well known, the fluorine molecule is unbound at the HF level. The bond distance optimized at this level is also too short indicating an excessive ionic character of the wavefunction. The calculated harmonic vibrational frequency is also too high evidencing the inadequate behavior of the energy in the vicinity of the HF equilibrium distance. At the GVB(1/2)-PP level, we get a positive binding energy that is still less than half of the experimental value. It is instructive to understand clearly what the GVB(1/2)-PP description is bringing to its particular molecule in order to make it bound. It is usually considered that the main effect of GVB(1/2)-PP is the inclusion of left–right correlation. This type of correlation is necessary for the dissociation of a two-electron bond in open-shell fragments, and is actually equivalent to the explicit description of the permutation symmetry of the electron coordinates in the bonding region. However, in the fluorine case the main effect of the GVB(1/2)-PP description is a striking modification in the charge distribution of the molecule in relation to the HF description. It was already noticed in the literature that the fluorine molecule has an electronic density deficit in the bonding region at the HF level [60, 61]. However, the main concern of these works was the description of chemical bonding through the analysis of difference densities between molecular and atomic densities. Here we are focused on the influence of specific correlation effects on the electronic structure of dihalogen molecules. We do not analyze the charge density itself, but a simpler charge density related quantity, the quadrupole moment. With this goal in mind, we have calculated the quadrupole moments of fluorine to probe the differences in the charge distribution in function of the level of calculation. Due to the symmetry of the molecule, only the axial component (2*ZZ*–*XX*–*YY*) of the quadrupole moment is non-zero.

As shown in Table 2, there is a difference of more than a 100% between the quadrupole moment as calculated at the

HF and GVB(1/2)-PP levels. Roughly speaking, in the case of a homonuclear diatomic molecule the *ZZ* component informs on the relative charge density on the atoms, and the *XX* and *YY* components on the relative charge density on the center of mass, which is in the middle of the bonding region. One sees that the HF wavefunction describes poorly the electron concentration in the bonding region, and that this effect is largely adjusted in the simple GVB(1/2)-PP description. This readjustment is so significant that there is a difference of 43.7 kcal/mol in the BDE associated with these two wavefunctions, a difference larger than the experimental BDE itself. Note that we are not associating chemical bonding with charge concentration in the bond region. We are simply remarking that the HF charge density is extremely inaccurate and the use of the simple GVB(1/2)-PP wavefunction provides a major improvement in the description of that property. Another indication of the remarkable changes of the wavefunction at the GVB(1/2)-PP level in relation to the HF level is provided by the vibrational harmonic frequency. At the HF level it is 300 cm^{-1} larger than the experimental value. At the GVB(1/2)-PP it is 200 cm^{-1} lower than the experimental value. In spite of the much improved description of the charge density, the BDE calculated at the GVB(1/2)-PP level is still very low. The next meaningful GVB-PP wavefunction includes all valence electron pairs in the active space. We have performed full-valence GVB(7/14)-PP and GVB(7/21)-PP calculations obtaining the same disappointing results. Both GVB-PP wavefunctions also do not really improve the value of the harmonic vibrational frequency in relation to the simplest GVB(1/2)-PP level. In the GVB(7/14)-PP description each valence electron pair is represented by two natural orbitals bringing only a marginal improvement in the BDE. In the GVB(7/21)-PP description, three natural orbitals are used to represent each valence electron pair. In this case the results of BDE are even worse than the ones obtained with the two other simpler GVB-PP wavefunctions. A third orbital in a SO-GVB-PP calculation improves the description of the electron–electron cusp, being a step towards the inclusion of intra-pair dynamic correlation. The disappointing result of the SO-GVB(7/21)-PP binding energy can be taken as an indication of the relatively minor importance of intra-pair dynamic correlation in the BDE of fluorine. The optimized bond distances for all GVB-PP wavefunctions are also too long. In the classical VB framework these results are usually rationalized within the concept of lone-pair-bond-weakening-effect (LPBWE) [2, 62, 63]. It is considered that this effect is due to repulsions between the bonding electrons and the lone pairs described by orbitals bearing the same symmetry of the bond. The improper treatment of these interactions results in lower binding energies and longer bond distances. In VB language, it arises due to an unbalance between covalent and ionic structures. In BOVB calculations, the proper balance is attained by superposing the covalent and ionic structures. As explained above the most important Hamiltonian term in this respect is the interaction between the covalent and ionic structures. The GVB-PP Hamiltonian includes all the features associated with the covalent and ionic component of a two-electron bond but it misses some effects associated with the interaction between covalent and ionic components. Although this fact presents no problem in the qualitative description of systems without valence lone electron pairs, we have just verified that in the case of fluorine important physical effects are missing. If we want to properly describe the binding energy and bond distance of the fluorine molecule in the GVB theoretical framework it is necessary to improve it beyond the perfect-pairing approximation. Therefore, we reinforce the findings of Shaik e Hiberty concerning the limitations of the perfect-pairing approximation in the qualitative description of the bonding in the fluorine molecule [8].

In Table 1, we see that the GVB-RCI wavefunction recovers most of the binding energy of the fluorine molecule improving considerably upon the GVB-PP results. This fact is more significant if one realizes that the dynamic correlation (in the Coulomb hole sense) is still missing. We are not claiming that dynamic correlation effects are not important for the description of the electronic structure of the fluorine molecule. However, its binding energy seems to be much less dependent on dynamic correlation than is usually considered. An indication that this is not a calculation artifact is the very accurate bond distance obtained at the GVB-RCI level. Actually, it is the closest to the experimental bond distance among all levels of calculation considered here. The GVB-RCI wavefunction also yields the best value for the harmonic vibrational frequency. Additionally, one should note that the quadrupole moment calculated at the GVB-RCI level is essentially the same as the ones calculated at CASSCF and MP2 levels. This means that the charge distribution should be accurately represented. In physical terms, the main difference between a GVB-PP calculation and a GVB-RCI calculation is the description of interpair charge correlations [38]. More than 20 years ago in a study of differential correlation effects on the description of the OH radical and anion, Chipman [64] recognized the importance of the interpair charge correlations as described by a GVB-RCI wavefunction. Note that the OH radical and anion species are respectively isoelectronic with the fluorine atom and anion. In Table 3, it is shown the most important configurations in the GVB-RCI wavefunction expressed in the optimized natural orbital basis.

Besides the reference, the two most important spatial configuration corresponds to the intrapair “sigma” and

Table 3 Most important excitations in relation to the reference (coefficient = 0.967777) in the converged GVB-RCI(7/14) wavefunction for the fluorine molecule defined in the optimized natural orbital basis

Excitation	Type	Coefficient
$\sigma_g^2 \rightarrow \sigma_u^2$	Connected double	−0.197380
$p_{x,y}^2 \rightarrow p_{x,y}^{2*}$	Connected double	4 × −0.04465
$p_x^2 \rightarrow p_x^1 p_x^{1*}$ $p_y^2 \rightarrow p_y^1 p_y^{1*}$	Disconnected double (singlet ⊗ singlet)	4 × −0.03183
$p_{x,y}^2 \rightarrow p_{x,y}^1 p_{x,y}^{1*}$ $\sigma_g^2 \rightarrow \sigma_g^1 \sigma_u^1$	Disconnected double	8 × −0.02739
$p_{x,y}^2 \rightarrow p_{x,y}^1 p_{x,y}^1$ $s_{\mathrm{A,B}}^2 \rightarrow s_{\mathrm{A,B}}^1 s_{\mathrm{A,B}}^{1*}$	Disconnected double	8 × −0.02495
$p_x^2 \rightarrow p_x^1 p_x^{1*}$ $p_y^2 \rightarrow p_y^1 p_y^{1*}$	Disconnected double (triplet ⊗ triplet)	4 × −0.02466

lone "pi" pair double excitations already present in the GVB-PP(7/14) wavefunction. In principle, the description of simple electrostatic lone pair repulsions at the GVB-PP level should be similar or slightly better than the one at the HF level [65]. However, these levels are unable to describe electronic repulsions due to simultaneous charge fluctuation in different electron pairs. To properly describe repulsion due to charge fluctuations in the present basis, we must have even order disconnected clusters of single excitations. They correspond to simultaneous charge polarization in different regions of the molecule and are the next important terms in the GVB-RCI linear expansion. Note that they are particularly related to the "*p*-like" lone pairs in different fluorine atoms and their influence on the bonding electrons. In order to establish that the most important lone pair repulsions are between "*p*-like" lone pairs we have performed two GVB-RCI calculations with reduced active spaces. The results are presented in Table 4.

In the first one the four lone pair "*p*-like" orbitals were taken out of the active space, and the sigma bond orbitals and the two "*s*-like" lone pairs were retained in the GVB-RCI(3/6) active space. In the second one, the two "*s*-like" lone pairs were taken out of the active space, and the sigma bond orbitals and the four "*p*-like" lone pairs were retained in the active space of the GVB-RCI(5/10) calculation. The results in Table 4 clearly show that the repulsion due to charge fluctuation among the four "*p*-like" lone pairs is the key interaction in the description of the charge-shift bonding in fluorine.

Table 4 Absolute energies (a.u.) for optimized equilibrium geometries and dissociated atoms, bond dissociation energy (kcal/mol), optimized bond distance (Å) and harmonic vibrational frequency (cm^{-1}) for the F$_2$ molecule

	E_{req}	E_{diss}	D_{e}	r_{eq}	ν
GVB-RCI(3/6)	−198.850589	−198.827342	14.6	1.474	663
GVB-RCI(5/10)	−198.938746	−198.888779	31.4	1.423	880

In the GVB-RCI(3/6) wavefunction the "*p*-like" lone pairs are left out of the active space. In the GVB-RCI(5/10) wavefunction the "*s*-like" lone pairs are left out of the active space. All calculations performed with the aug-cc-pVTZ basis set

The influence of the lone pair repulsion in the binding energy of the fluorine molecule had been ingenuously demonstrated in spectroscopic experiments of Jolly and Eyermann [66]. These repulsions are not associated with short range electron–electron interactions being unrelated to the electron–electron cusps [67]. They are described by the simultaneous charge polarizations present in the full-valence, orbital optimized GVB-RCI wavefunction. Their inclusion is essential to the proper description of the BDE of the fluorine molecule. The lone pair repulsion readjustment induced by extra terms in the GVB-RCI expansion allows this wavefunction to yield acceptable values of binding energy, bond distances and even harmonic vibrational frequencies. The GVB-RCI provides the best value for the harmonic frequency for the fluorine molecule presenting a fair description of the concavity of the potential energy surface (PES). These results are evidence of the special nature of the electronic correlation in the fluorine molecule since all of them were achieved without the inclusion of dynamic correlation in the Coulomb hole sense. Hence, we can picture the charge-shift effect in the fluorine molecule as initially resulting from simultaneous charge density polarizations induced by lone pair repulsions. The proper account of the fluctuations on the lone pair electronic densities allows the fluorine atoms to become closer increasing the BDE. In Table 3 we can see the combined charge relaxation among the "*p*-like" lone electron pairs and the bonding "sigma" and "*s*-like" electron pairs. Since fluorine is a homonuclear diatomic molecule, it is expected that net charge transfer effects are relatively unimportant. The remaining improvements in the wavefunction should be of lesser importance and must be associated with the proper description of the electron–electron cusps, i.e. ordinary dynamic correlation.

The next level of description of the electronic structure of the fluorine molecule is the CASSCF(14,14) wavefunction. The comparison between the GVB-RCI and the CASSCF wavefunctions provides an indication of the influence of valence charge transfer configurations in the electronic structure of the fluorine molecule. In Table 1 it is seen that the CASSCF(14,14) level overestimates the fluorine binding energy by about 2.1 kcal/mol. It is known that the CASSCF wavefunction including all valence orbitals is necessarily size consistent. And considering that the binding energies were taken as differences between bound and dissociated system we must conclude that the energy associated with the equilibrium distance is too low. Using the constrained-CASSCF wavefunction defined above at the CASSCF bonding distance we verify that the energy lowering due to charge transfer among different fluorine atoms amount to 7.9 kcal/mol. It should be noted that this charge transfer associated energy is essentially the difference in binding energy between the GVB-RCI and CASSCF levels. One possible qualitative explanation for this effect is the so-called "anionic character" of the fluorine atom [68]. At near equilibrium distances, charge transfer configurations may acquire an unphysical large importance in an attempt to describe dynamic correlation effects in a limited orbital space. Once the atoms are distant from each other genuine charge transfer effects must be completely negligible. This is true even for heteronuclear bonds, because at long distances orbital overlap and ionic attraction are null and all ionization potentials are larger in module than any electron affinity. To properly describe the electron–electron cusp with CI-type wavefunctions one needs to access a much larger orbital basis, the GVB-RCI natural orbitals being clearly insufficient for this purpose. The extremely large differences observed in the description of the fluorine molecule in moving from GVB-PP to GVB-RCI wavefunctions are an indication that pair repulsions are much more important than changes of shape in the valence natural orbitals. Hence, we are led to conclude that charge transfer effects are likely to be an unphysical side effect of the too tight character of the fluorine valence natural orbitals. Additionally, the optimized bond distance at the CASSCF(14,14) level is too short indicating an excessive ionic character in the wavefunction. Although the quadrupole moment at the CASSCF level is equivalent to the one calculated at the more balanced GVB-RCI level, it is well known that the relative importance of ionic–covalent character is completely blurred when looking to charge density related quantities only [69]. These facts provide a clue to understand why the BOVB approach works so well for the fluorine molecule. In the BOVB approach, the superposition of covalent and ionic structures allows a fair description of the charge variation function along the molecule. Through the ionic structures the anionic character of the fluorine atom and the lone pair repulsions between fluorine atoms are put into balance through the size variation of the lone pairs. The final effect is an unspecified mixture of physical effects that succeeds in describing the chemical bond in the fluorine molecule.

The inclusion of dynamic correlation through an MP2 calculation brings some improvement on the binding energy in relation to the GVB-RCI result. However, the bond distance optimized at the MP2 level is too short. This disappointing performance is probably related to the fact that MP2 calculations use the HF determinant as reference. As already shown above, at the HF level the fluorine molecule is unbound and its charge density is extremely inaccurate. The canonical HF orbital basis obviously cannot play the part of a "correct" first order reference for the subsequent MP2 treatment. The excessive ionic bias of the orbital basis may cause the bond shortening at the MP2 level.

The incorporation of left–right correlation in the reference for the perturbation treatment through the MR-MP2 approach takes the binding energy closer to the experimental result. However, the bond distance is now too long. This is probably related to some unbalance in the treatment of the lone pair repulsions. We have shown above that a fair account of the lone pair repulsions is provided by a full-valence GVB-RCI approach, which actually comprises 70392 determinants in a linear CI-type expansion with localized optimized orbitals. The success of the GVB-RCI approach for the fluorine molecule is also in line with the fact that sometimes a localized natural orbital basis may have optimal convergence properties in a proper CI expansion [70]. As noted by other authors using multi-reference-CI approaches, the use of only two references is in general insufficient for the success of the correlation treatment. The recent very accurate studies at the multi-reference CI level [71–74] demonstrated the importance of the flexibility of the reference space in the description of potential energy curves for the fluorine molecule.

5.2 Chlorine and bromine

The general trends followed by these two molecules are similar and can be discussed together. The bond dissociation energies (BDE), optimized bond distances, harmonic vibrational frequencies and quadrupole moments at each level of calculation for the chlorine and bromine molecules are presented on Tables 5, 6.

In contrast to fluorine, both molecules are bound at the HF level. The accurate optimized bond distances obtained at the HF level are probably due to a fortunate set of canceling errors. Their quadrupole moments at this level are not very different from the ones calculated at the more complete levels. For both molecules, left–right correlation effects at the equilibrium distance increase the electron density in the

Table 5 Absolute energies (a.u.) for optimized equilibrium geometries and dissociated atoms, bond dissociation energy (kcal/mol), optimized bond distance (Å) and harmonic vibrational frequency (cm^{-1}) for the Cl_2 molecule at different levels of calculation

	E_{req}	E_{diss}	D_{e}	r_{eq}	v
HF	−919.000062	−918.960397	24.9	1.984	610
GVB(1/2)-PP	−919.021333	−918.960397	38.2	2.047	501
GVB(7/14)-PP	−919.044135	−918.983617	38.0	2.048	563
GVB(7/21)-PP	−919.061963	−919.000147	38.8	2.037	483
GVB-RCI(7/14)	−919.089813	−919.019532	44.1	2.024	537
CASSCF(14,14)	−919.148880	−919.072827	47.7	2.027	524
MP2-frozen core	−919.387079	−919.309671	48.6	1.999	573
(2,2)MR-MP2	−919.389840	−919.309671	50.3	2.032	538
Experimental [1]			58.0	1.988	560

All calculations performed with the aug-cc-pVTZ basis set

Table 6 Absolute energies (a.u.) for optimized equilibrium geometries and dissociated atoms, bond dissociation energy (kcal/mol), optimized bond distance (Å) and harmonic vibrational frequency (cm^{-1}) for the Br_2 molecule at different levels of calculation

	E_{req}	E_{diss}	D_{e}	r_{eq}	v
HF	−5144.915940	−5144.880936	22.0	2.276	354
GVB(1/2)-PP	−5144.935526	−5144.880936	34.3	2.341	294
GVB(7/14)-PP	−5144.954865	−5144.899612	34.7	2.344	294
GVB(7/21)-PP	−5144.967372	−5144.912807	34.2	2.342	315
GVB-RCI(7/14)	−5144.985158	−5144.929300	35.1	2.330	306
CASSCF(14,14)	−5145.036901	−5144.972545	40.4	2.328	308
MP2-frozen core	−5145.244288	−5145.175594	43.1	2.289	337
(2,2)MR-MP2	−5145.248664	−5145.175594	45.8	2.316	310
Experimental [1]			45.9	2.28	325

All calculations performed with the aug-cc-pVTZ basis set

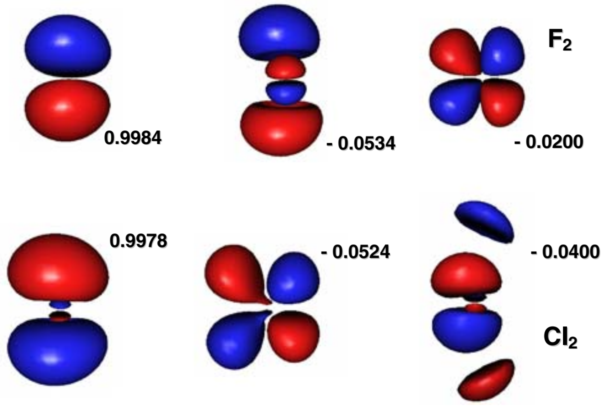

Fig. 1 Orbitals and expansion coefficients for the *p*-like lone electron pair in the GVB(7/21)-PP wavefunctions for fluorine and chlorine molecules. In this wavefunction, each valence electron pair is uniquely described by three orthogonal natural orbitals

bonding region, but to a much lesser extent than in the fluorine molecule. Thus, the inclusion of electronic correlation does not change appreciably the charge density associated with these molecules. The incorporation of left–right correlation gives an increment of about 43.7 kcal/mol in the BDE for the fluorine molecule. While for the chlorine and bromine molecules this increment is much smaller being, respectively, 13.3 and 12.3 kcal/mol. The extension to the SO-GVB-PP wavefunction including all valence pairs brings no significant improvement in the BDE of the chlorine and bromine molecules. Additionally, since also the bond distances optimized at the GVB-PP levels are all too long we can deem the very good harmonic frequencies results at the GVB(7/14)-PP level for chlorine and at the GVB(7/21)-PP level for bromine as purely accidental.

At the GVB-RCI level, there is an improvement of 5 kcal/mol in the BDE of the chlorine molecule. For the bromine molecule this improvement is much smaller, being less than 1 kcal/mol. The BDEs calculated with the GVB-RCI wavefunction provide an assessment of the importance of interatomic interpair charge fluctuation repulsions for the chlorine and bromine molecules. These results are in accordance with the expectation of relatively low importance of interatomic charge fluctuation lone pair repulsions in the description of the electronic structure of these molecules [66]. This is to be contrasted with the large importance of this mode of repulsion in the fluorine molecule.

In order to access the possible reasons for the different electronic behavior of fluorine in relation to chlorine and bromine molecules, we will consider two complementary results that rose from the calculations. Firstly, we compare the description of the "*p*-like" lone pair electronic correlation at the GVB(7/21)-PP level for fluorine, chlorine and bromine molecules. In Fig. 1, we see the three orthogonal natural orbitals with their respective coefficients in the GVB(7/21)-PP expansion for fluorine and chlorine.

The bromine orbitals and coefficients are not shown since they are similar to the chlorine ones. The fluorine "*p*-like" lone pair orbitals have no valence correlating orbital in the same region of space. If intrapair correlation effects were dominant, one should expect the second larger coefficient in the GVB(7/21)-PP expansion for this pair to be associated with a small "*d*-like" natural orbital. That would maximize the two-electron exchange with the doubly occupied "*p*-like" orbital. However, the most important correlation effect within this electron pair is brought by a larger "*p*-like" orbital describing the radial displacement of the electrons away from the molecule axis. Since an interpair repulsion prevails over the intrapair correlation in a variational calculation we may conclude that the "*p*-like" orbital that describes the lone electron pairs must be extremely tight. This result fits neatly within the idea that in the fluorine molecule the mutual repulsion of the "*p*-like" lone pairs is an unusually important differential correlation effect in the molecule formation. For chlorine and bromine the most important correlation effect within this electron pair is brought by a valence "*d*-like" orbital describing its longitudinal displacement along the molecule axis. In this case the electron pair is not "driven away" from the molecule but it instead splits itself along the molecule axis, as expected for an intrapair correlation effect. These findings should be complemented by an analysis of the influence of charge transfer effects on the energies of chlorine and bromine at their optimized bond distances. We have already discussed above our model for the influence of interatomic charge transfer effects applied to the fluorine molecule. Analogously the energetic effect of interatomic charge transfer in chlorine and bromine is taken as the energy difference between the full CASSCF(14,14) and a constrained-CASSCF(14,14) where no net interatomic charge transfer is allowed. For fluorine we concluded that this effect was small (7.8 kcal/mol) and possibly spurious since at this level the molecule was overbound. In chlorine and bromine the effect observed is significantly larger, being, respectively, 33.5 and 31.5 kcal/mol. In physical terms the energetic importance of charge transfer determinants in the CASSCF wavefunction in homonuclear molecules is an indication of interatomic charge density interpenetration. It is well known that when two charge densities of the same sign interpenetrate their repulsion is relieved. Until the GVB-RCI level we have worked under a strict electron pair exclusion principle. At these levels "lone pair repulsion" is strictly equivalent to "Pauli repulsion". At the CASSCF level, we lift the electron pair exclusion principle restriction. Thus, the associated energy stabilization should be related to a decrease in lone pair repulsion due to charge density interpenetration. This idea is not new and we will return to it when comparing our results with others in the literature. It should be clear that the fluorine orbitals are too tight to allow charge density interpenetration and this fact alone can respond for its anomalous properties.

The inclusion of electronic correlation through a MP2 calculation improves the results for both chlorine and bromine. Bond distances and harmonic vibrational frequencies are well reproduced indicating that HF canonical orbitals provide a reasonable basis for the MP2 calculation. The subsequent step of a MR-MP2 improves the binding energies and slightly deteriorates the results for bond distances and harmonic vibrational frequencies. These results suggest that there is nothing unusual in the electronic correlation mode of chlorine and bromine molecules. While the fluorine molecule has an unique electronic structure with a prevalence of lone pair charge fluctuations, chlorine and bromine present an ordinary dependence of their properties in function of the inclusion of electronic correlation. The large importance of covalent-ionic resonance found in BOVB calculations for chlorine may be attributed to the limited basis sets used in those calculations [6–9, 15–17]. It is already known that basis set restrictions and overly simplified models can compromise the qualitative interpretation of the bonding mode in special circumstances [75]. In conclusion, we point out that from the perspective developed here there is no evidence of anything similar to "charge-shift-bonding" in the electronic structure of chlorine and bromine molecules.

6 Comparison to other approaches

The process of understanding the chemical bonding from ab initio calculations always falls into one of two possible different philosophies. The most common one is to use some model of analysis of the wavefunction (or wavefunction related property) which is unrelated to the process of generating it. Typical examples are the theories that try to understand chemical bonding through the analysis of the charge density [76–78]. To say the least, what is usually overlooked is that the charge density has to be generated from a wavefunction (or parametrized density functional), and depending on the particular situation the method employed may provide a spurious density. The other approach consists in using effective and/or approximate Hamiltonians associated with a given physical or chemical model. The subsequent improvement of the Hamiltonian in a controlled way indicates the relative importance and role of different physical effects in the formation of the chemical bond [79–82]. In the present paper, a novel path within the philosophy the latter approach has been followed. In the light of our results, we will analyze some of the other approaches existent in the literature applied to dihalogen molecules.

The first qualitative explanation for the low BDE of fluorine came from Mulliken [83]. In his paper, it was presented the idea that it is not the BDE of fluorine that is too low but the BDEs of the other dihalogen molecules that are too high. The reason for that it would be an increased multiple bonding character from chlorine to iodine due to participation of unoccupied "d" orbitals. Indeed, as shown above the main difference between fluorine and the other halogens is the mode of the electronic correlation in the "p" lone pairs due to the increased importance of the "d-type" correlation natural orbitals for chlorine and bromine. However, in order to properly relate this feature to multiple bonding character it would be necessary to have another form of spin coupling with a comparable weight than the one associated with the main spin eigenfunction

[24–30]. This is clearly not the case as can be inferred from the large dominance of the leading term coefficient in the natural orbital GVB-PP expansion for the "*p*-like" lone pairs.

The first quantitative attempt to explain the apparent anomalous BDE of fluorine was due to Pitzer [84]. Somewhat in the line of Mulliken he suggested that the BDE of the dihalogen molecules, with the exception of fluorine, had an appreciable attractive dispersion component. With a very approximate model he calculated the attractive dispersion energy and found out that this procedure eliminates much of the "anomaly" of the sequence of BDEs. Caldow and Coulson [85] repeated the calculations of Pitzer using a more elaborated model with updated values of atomic polarizabilities and disregarded his hypothesis. Both calculations ignored lone pair overlap and orbital optimization effects. They also admitted that the polarizability of the isolated atom is maintained in the molecule. With the present state of evolution of ab initio calculations it should be clear that these calculations have a limited conceptual value.

Pauling [5] suggested that the possibility of some amount of hybridization (mixing) of the "*p*-like" lone pairs with "*d*-like" orbitals should contribute to alleviate the lone pair repulsions. This effect would not take place for the fluorine molecule. Hence, the reduced BDE of the fluorine molecule would stem from an excessive amount of "*p*-like" lone pair repulsion. This explanation is in line with the main results of the present paper. It is also the preferred explanation in textbooks of Inorganic Chemistry [86]. However, it had always needed to be developed further in order to prove its consistency. We believe that we have provided sufficient evidence here to support and refine the original proposition from Pauling.

The description of the fluorine molecule bonding from the analysis of the charge density has been plagued by the difficulty of obtaining a reliable description for this system from density functional theory (DFT) [87, 88]. Even so, three recent studies using a DFT-based energy decomposition analysis (EDA) [77] to analyze bonding in dihalogen molecules have concluded that an anomalously low amount of electrostatic attraction is responsible for the low BDE of fluorine molecule [88–90]. Within their EDA scheme it was found out that "Pauli repulsions" keep the fluorine atoms from getting closer. Hence, they experience a lesser amount of electrostatic attraction. It must be stressed that the main explanations presented in these papers [88–90] are bound to the EDA method assumptions and approximations. However, their final conclusions are somewhat in line with our results. An electron-localization-function (ELF) approach was employed in systems considered to present charge-shift bonding [15]. It was concluded that the charge-shift effect manifests itself through a depleted electronic density in the bond region. We must point out that we have calculated the quadrupole moment of fluorine molecule with dozens of pure and hybrid density functionals available in the GAMESS package, and they have always underestimated the charge density in the middle of the molecule. We have already shown above that the simple GVB(1/2)-PP largely corrects the charge density of the fluorine molecule in relation to the HF reference. Since at the GVB(1/2)-PP level the charge-shift bond effect is not operative we must conclude that the existence of depleted electron density in a molecule bond region is not an appropriate criteria. In an atoms-in-molecules (AIM) based study it was pointed out that the bonding in fluorine has a very low degree of covalency [91]. Although the authors properly took care of left–right correlation effects through GVB(1/2)-PP and CASSCF(6,6) wavefunctions they have completely missed the influence of charge fluctuation in the "*p*-like" lone pairs. In the present paper we have clearly shown that this is the key differential correlation effect responsible for the unique features of fluorine molecule bonding. On the other hand they realized the importance of considering also two-particle densities in an analysis of chemical bonding, which is particularly essential in the specific case of the fluorine molecule as exhaustively shown here.

7 Summary and conclusions

In this paper, we analyzed the electronic structure of the fluorine, chlorine and bromine molecules using a variety of GVB wavefunctions. It should be remarked that as far as the authors are concerned these are the first published GVB study in which the complete set of halogen valence lone pairs are included in the active space. It has been suggested in the literature that the bonding in the fluorine and chlorine molecules are of a special kind named "charge-shift bonding". It has also been argued in the literature that perfect-pairing (PP) GVB wavefunctions would be unable to describe qualitatively the charge-shift bonded systems. In the present paper, we have tried to verify these statements using GVB-PP wavefunctions that include the complete valence space. We have also increased the number of natural orbitals per electron pair and eliminated the perfect-pairing restriction through an orbital optimized GVB-RCI wavefunction. Our goal was to establish if these wavefunctions would be able to put in evidence some electronic characteristic of these systems that could justify the need for the concept of "charge-shift bonding".

Through quadrupole moment calculations we found out a huge difference between the HF and the GVB(1/2)-PP charge densities for the fluorine molecule. Thus, the long known fact that the fluorine molecule is unbound at the HF level was shown to be correlated to a spurious depleted charge density in the bond region. This fact was already noted in literature [15, 60, 61]. We have shown here that the simple GVB(1/2)-PP wavefunction actually corrects the quadrupole moment bringing it to values close to those obtained from more sophisticated wavefunctions. However, all GVB-PP wavefunctions considered (GVB(1/2)-PP, GVB(7/14)-PP and GVB(7/21)-PP) largely underestimated the BDE, yielded too long optimized bond distances and poor values for harmonic vibrational frequencies. As expected, the GVB-PP approach is unable to describe qualitatively the electronic structure of the fluorine molecule. The situation dramatically changes for the GVB-RCI wavefunction. By lifting the perfect-pairing restriction including in a variational way all disconnected clusters of single excitations within an orbital pair, we have obtained very good values for the BDE, optimized bond distance and harmonic vibrational frequency. Additionally, we were able to associate "charge-shift bonding" with an anomalously large importance of charge fluctuation lone pair repulsions. The most striking fact was that we were able to describe these features of the fluorine molecule without including ordinary dynamic correlation, i.e. without accurately describing the electron–electron cusp. In the behavior of the chlorine and bromine molecules under the same conditions it was not possible to note anything out of the ordinary. In general, these two systems present the expected dependence on the description of electronic correlation to improve the value of properties calculated. The anomalous characteristics of the fluorine molecule are argued to be related to the extremely compact nature of its valence orbitals. This feature prevents charge density interpenetration effects that would contribute to relieve the amount of "*p*-like" lone pair repulsions. This lone pair repulsion "excess" explains the somewhat long bond distance of the fluorine molecule and why the BDE increases from fluorine to chlorine.

There are many relevant conclusions that may be drawn from the present work.

- HF charge density for the fluorine molecule is extremely inaccurate. This fact causes the HF canonical orbital basis for this system to be inadequate in low order correlation treatments in spite of the fact that there are no "near degeneracies" at the equilibrium distance.
- Even the simplest GVB-PP wavefunction is able to correct the charge density of the fluorine molecule from the HF result.
- Charge-shift bonding effects cannot be described within the perfect-pairing restriction, even if we include all the valence electrons in the active space.
- Charge-shift bonding is an intrinsically two-particle effect and cannot be directly pictured with charge density related quantities.
- Within our approach, the charge-shift bonding effect is associated with an anomalously large importance of charge fluctuation lone pair repulsions
- The inclusion of all valence disconnected clusters of single excitations associated with an orbital optimized GVB-RCI wavefunction succeeds in describing the charge-shift bonding effect and the properties calculated for the fluorine molecule.
- Dynamic correlation effects in the Coulomb hole sense have a lesser importance in the description of the electronic structure and properties of the fluorine molecule than is usually considered.
- The essential electron pairs for the description of the charge-shift bonding effect are the ones perpendicular to the bond axis.
- Within our approach, the charge-shift bonding concept is meaningful only for the fluorine molecule. The attribution of this effect for the chlorine molecule bond should be related to the limited size of the basis sets used in the BOVB calculations.
- Admitting the soundness of our model, no elements located below the second row (Li–Ne) of the periodic table would present the effects that we have associated with charge-shift bonding.

Acknowledgments The authors would like to thank Mr. Felipe P. Fleming and Prof. Marco A. C. Nascimento for helpful discussions on the subject of this paper. Financial support from PROPP-UFF, Faperj and CNPq is acknowledged.

References

1. Huber KP, Herzberg G (1979) Molecular spectra and molecular structure, IV. Constants of diatomic molecules. Van Nostrand Reinhold, New York
2. Shaik S, Maitre P, Sini G, Hiberty PC (1992) J Am Chem Soc 114:7861. doi:10.1021/ja00046a035
3. Raimondi M, Simonetta M, Tantardini GF (1985) Comput Phys Rep 2:171. doi:10.1016/0167-7977(85)90008-5
4. McWeeny R (1992) Methods of molecular quantum mechanics. Academic Press, London
5. Pauling L (1960) The nature of the chemical bond, 3rd edn. Cornell University Press, Ithaca
6. Hiberty PC, Flament JP, Noizet E (1992) Chem Phys Lett 189:259. doi:10.1016/0009-2614(92)85136-X
7. Hiberty PC, Humbel S, Byrman CP, van Lenthe JH (1994) J Chem Phys 101:5969. doi:10.1063/1.468459
8. Shaik S, Hiberty PC (2002) In: Cooper DL (ed) Valence bond theory. Elsevier, Amsterdam
9. Hiberty PC, Shaik S (2002) Theor Chem Acc 108:255. doi:10.1007/s00214-002-0364-8
10. Li J, McWeeny R (2002) Int J Quantum Chem 89:208. doi:10.1002/qua.10293
11. Li J, Duke B, McWeeny R (2006) VB2000 v. 1.8(R2). SciNet Technologies, San Diego
12. McDouall JJW (1992) Theor Chim Acta 83:339. doi:10.1007/BF01113060

13. McDouall JJW (1993) Theor Chim Acta 85:395. doi:10.1007/BF01113433
14. McDouall JJW (2002) In: Cooper DL (ed) Valence bond theory. Elsevier, Amsterdam
15. Shaik S, Danovich D, Silvi B, Lauvergnat DL, Hiberty PC (2005) Chem Eur J 11:6358. doi:10.1002/chem.200500265
16. Hiberty PC, Megret C, Song L, Wu W, Shaik S (2006) J Am Chem Soc 128:2836. doi:10.1021/ja053130m
17. Hiberty PC, Ramozzi R, Song L, Wu W, Shaik S (2007) Faraday discuss 135:261. doi:10.1039/b605161h
18. Goddard WAIII, Dunning TH, Hunt WJ, Hay PJ (1972) Acc Chem Res 6:368. doi:10.1021/ar50071a002
19. Heisenberg W (1926) Z Phys 38:411. doi:10.1007/BF01397160
20. Heisenberg W (1926) Z Phys 39:501
21. Wigner E (1926) Z Phys 40:883
22. Heitler W, London F (1927) Z Phys 44:445
23. Coulson CA, Fischer I (1949) Philos Mag 40:383
24. Goddard WAIII (1967) Phys Rev 157:73. doi:10.1103/PhysRev.157.73
25. Goddard WAIII (1967) Phys Rev 157:81. doi:10.1103/PhysRev.157.81
26. Goddard WAIII (1968) J Chem Phys 48:450. doi:10.1063/1.1667943
27. Goddard WAIII (1968) J Chem Phys 48:5337. doi:10.1063/1.1668225
28. Goddard WAIII, Ladner RC (1969) J Chem Phys 51:1073. doi:10.1063/1.1672106
29. Gerratt J (1971) Adv At Mol Phys 7:141
30. Cooper DL, Gerratt J, Raimondi M (1987) Adv Chem Phys 69:319. doi:10.1002/9780470142943.ch6
31. Goddard WAIII, Harding LB (1978) Annu Rev Phys Chem 29:363. doi:10.1146/annurev.pc.29.100178.002051
32. Cooper DL, Gerratt J, Raimondi M (1991) Chem Rev 91:929. doi:10.1021/cr00005a014
33. Gerratt J, Cooper DL, Karadakov PB, Raimondi M (1997) Chem Soc Rev 26:87. doi:10.1039/cs9972600087
34. Bobrowicz FW, Goddard WA III (1977) In: Schaeffer HF (ed) Methods of electronic structure theory. Plenum Press, New York
35. Arai T (1960) J Chem Phys 33:95. doi:10.1063/1.1731142
36. Hurley AC, Lennard-Jones J, Pople JA (1953) Proc R Soc A 220:446. doi:10.1098/rspa.1953.0198
37. Surján PR (1999) Top Curr Chem 203:63. doi:10.1007/3-540-48972-X_4
38. Shepard R (1987) Adv Chem Phys 69:63. doi:10.1002/9780470142943.ch2
39. Matsen FA (1964) Adv Quantum Chem 1:59. doi:10.1016/S0065-3276(08)60375-5
40. Matsen FA (1970) J Am Chem Soc 92:3525. doi:10.1021/ja00715a001
41. Yaffe LG, Goddard WAIII (1976) Phys Rev A 13:1682. doi:10.1103/PhysRevA.13.1682
42. Dunning TH, Cartwright DC, Hunt WJ, Hay PJ, Bobrowicz FW (1976) J Chem Phys 64:4755. doi:10.1063/1.432062
43. Bobrowicz FW (1981) In Dupuis M (ed) Recent developments and applications of multiconfigurational Hartree-Fock methods. NRCC, Lawrence Berkeley Laboratory, University of California, Berkeley
44. Carter EA, Goddard WAIII (1988) J Chem Phys 88:3132. doi:10.1063/1.453957
45. Faglioni F, Goddard WAIII (1999) Int J Quantum Chem 73:1. doi:10.1002/(SICI)1097-461X(1999)73:1<1::AID-QUA1>3.0.CO;2-0
46. Barbosa AGH, Fleming FP (unpublished)
47. Van Voorhis T, Head-Gordon M (2001) J Chem Phys 115:7814. doi:10.1063/1.1406536
48. Cullen J (1999) J Comput Chem 20:999. doi:10.1002/(SICI)1096-987X(19990730)20:10<999::AID-JCC2>3.0.CO;2-A
49. Roos BO (1987) Adv Chem Phys 69:399. doi:10.1002/9780470142943.ch7
50. Ruedenberg K, Cheung LM, Elbert ST (1979) Int J Quantum Chem 16:1069. doi:10.1002/qua.560160511
51. Roos BO, Taylor PR, Siegbahn PEM (1980) Chem Phys 48:157. doi:10.1016/0301-0104(80)80045-0
52. Levy B, Berthier G (1968) Int J Quantum Chem 2:307. doi:10.1002/qua.560020210
53. Barbosa AGH, Nascimento MAC (2004) Int J Quantum Chem 99:317. doi:10.1002/qua.10866
54. Nakano H (1993) J Chem Phys 99:7983. doi:10.1063/1.465674
55. Schmidt MW et al (1993) J Comput Chem 14:1347. doi:10.1002/jcc.540141112
56. Ivanic J, Ruedenberg K (2001) Theor Chem Acc 106:399
57. Ivanic J (2003) J Chem Phys 119:9364. doi:10.1063/1.1615954
58. Pipek J, Mezey PG (1989) J Chem Phys 90:4916. doi:10.1063/1.456588
59. Peterson KA, Kendall RA, Dunning TH Jr (1993) J Chem Phys 99:9790. doi:10.1063/1.465461
60. Schwarz WHE, Ruedenberg K, Mensching L, Miller LL, Valtazanos P, von Niessen W (1989) Angew Chem Int Ed Engl 28:597. doi:10.1002/anie.198905971
61. Mensching L, von Niessen W, Valtazanos P, Ruedenberg K, Schwarz WHE (1989) J Am Chem Soc 111:6933. doi:10.1021/ja00200a007
62. Sanderson RT (1983) Polar covalence. Academic Press, New York
63. Lauvergnat DL, Hiberty PC (1995) J Mol Struct Theochem 338:283. doi:10.1016/0166-1280(94)04067-3
64. Chipman DM (1986) J Chem Phys 84:1677. doi:10.1063/1.450464
65. Bitzer RS, Barbosa AGH, da Silva CO, Nascimento MAC (2005) Carbohydr Res 340:2171. doi:10.1016/j.carres.2005.07.001
66. Jolly WL, Eyermann CJ (1983) Inorg Chem 22:1566. doi:10.1021/ic00152a031
67. Davidson ER (1976) Reduced density matrices in quantum chemistry. Academic Press, New York
68. Taylor PR (2001) In Roos BO, Widmark PO (eds) European summer school of quantum chemistry. Lund University, Lund
69. Cook M, Karplus M (1987) J Phys Chem 91:31. doi:10.1021/j100285a010
70. Bytautas L, Ivanic J, Ruedenberg K (2003) J Chem Phys 119:8217. doi:10.1063/1.1610434
71. Ivanov VV, Adamowicz L, Lyakh DI (2006) Int J Quantum Chem 106:2875. doi:10.1002/qua.21113
72. Bytautas L, Nagata T, Gordon MS, Ruedenberg K (2007) J Chem Phys 127:164317. doi:10.1063/1.2800017
73. Bytautas L, Matsunaga N, Nagata T, Gordon MS, Ruedenberg K (2007) J Chem Phys 127:204301. doi:10.1063/1.2801989
74. Bytautas L, Matsunaga N, Nagata T, Gordon MS, Ruedenberg K (2007) J Chem Phys 127:204313. doi:10.1063/1.2805392
75. Ponec R, Yuzhakov G, Cooper DL (2004) Theor Chem Acc 112:419. doi:10.1007/s00214-004-0597-9
76. Bader RFW (1991) Chem Rev 91:893. doi:10.1021/cr00005a013
77. te Velde G, Bickelhaupt FM, Baerends EJ, van Gisbergen SJA, Fonseca Guerra C, Snijders JG, Ziegler T (2001) J Comput Chem 22:931. doi:10.1002/jcc.1056
78. Silvi B, Fourré I, Alikhani ME (2005) Mon Chem 136:855. doi:10.1007/s00706-005-0297-8
79. Ruedenberg K (1962) Rev Mod Phys 34:326. doi:10.1103/RevModPhys.34.326
80. Wilson CW Jr, Goddard WAIII (1972) Theor Chim Acta 26:195. doi:10.1007/BF00529306

81. Goddard WAIII, Wilson CW Jr (1972) Theor Chim Acta 26:211. doi:10.1007/BF00529307
82. Kutzelnigg W (1990) In: Maksic ZB (ed) Theoretical models of chemical bonding, vol 2. Springer, Berlin, p 1
83. Mulliken RS (1955) J Am Chem Soc 77:884. doi:10.1021/ja01609a020
84. Pitzer KM (1955) J Chem Phys 23:1735. doi:10.1063/1.1742443
85. Caldow GL, Coulson CA (1962) Trans Farad Soc 58:633. doi:10.1039/tf9625800633
86. Shriver DP, Atkins PW (1999) Inorganic chemistry, 3rd edn. Oxford University Press, New York
87. Koch W, Holthausen MC (2001) A chemists's guide to density functional theory, 2nd edn. Wiley-VCH, Weiheim
88. Forslund LE, Kaltsoyannis N (2003) N J Chem 27:1108. doi:10.1039/b301947k
89. Esterhuysen C, Frenking G (2004) Theor Chem Acc 111:381. doi:10.1007/s00214-003-0535-2
90. Krapp A, Bickelhaupt FM, Frenking G (2006) Chem Eur J 12:9196. doi:10.1002/chem.200600564
91. Rincón L, Alvarellos JE, Almeida R (2005) J Chem Phys 122:214104. doi:10.1063/1.1901564