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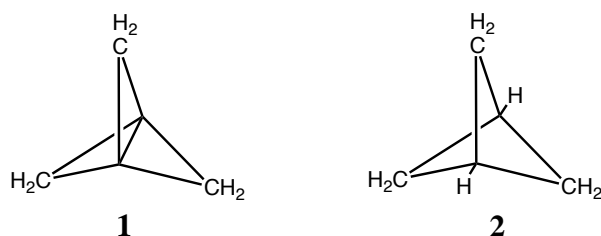
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Comment on “The ‘inverted Bonds’ revisited. Analysis of ‘in silico’ models and of [1.1.1]Propellane using Orbital Forces”

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In a recent publication in this journal, Laplaza, Contreras-Garcia, Fuster, Volatron and Chaquin^[1] (LCFVC) report an application of the Dynamical Orbital Forces (DOF) method,^[2] which was used by the authors to challenge the presence of an inverted central C-C bond in [1.1.1]propellane (**1** in Scheme 1), which was suggested long ago by Jackson and Allen,^[3] then by Feller and Davidson,^[4] and recently given theoretical support on the basis of ab initio valence bond calculations.^[5]



Scheme 1. The [1.1.1]propellane and bicyclo[1.1.1]pentane molecules

The DOF of a molecular orbital (MO) is the derivative of its energy with respect to distance between two atoms of the molecule. This quantity is interpreted, on the basis of Koopmans’ theorem, as the force exerted on the nuclei along this interatomic distance by removal of one electron from the MO, in the frozen MO approximation. The positive/negative sign of the

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DOF is used as a mean to characterize the bonding/antibonding nature of the MO with respect to the two atoms in question. As an extension of this model, the DOFs with respect to a given interatomic distance are summed over all the MOs (ϕ_i) of a molecule, and the result $\Sigma(\text{DOF}_i)$ is considered as the central quantity that determines the nature and strength of a particular bond. *A large positive $\Sigma(\text{DOF}_i)$ corresponds to a strong bond,^[1,6,7] while a negative $\Sigma(\text{DOF}_i)$ signifies a repulsive interaction.* This method was recently applied to a series of hydrocarbons and a linear correlation was found between the CC bonding energies and the CC $\Sigma(\text{DOF}_i)$.⁷

Back to [1.1.1]propellane **1** in Scheme 1: this cage molecule was long supposed to possess a significant σ bond between the two bridgehead carbons^[3,4] owing to its remarkably weak enthalpy of formation (only 143 kcal mol⁻¹) by extrusion of two hydrogen atoms from bicyclo[1.1.1]pentane **2**. This value is significantly smaller than twice the standard bonding energy of a C-H bond. The presence of this central σ bond in **1** was confirmed by *ab initio* calculations of the “breathing-orbital valence bond” (BOVB) type.^[5] These calculations confirmed the order of magnitude of ca. 60 kcal mol⁻¹, that was estimated in previous studies for this bond based on the above thermodynamic considerations.

Two features of the bridgehead bond in **1** are noteworthy: (i) the bonding interaction takes place between two sp³-like hybrid atomic orbitals (HAOs) pointing away from the center of the molecule, hence its description as an “inverted bond” ; (ii) at variance with classical covalent bonds, the bonding strength of the bridgehead CC bond is mostly due to the stabilizing resonance interaction, $\text{C}\cdot\text{---}\cdot\text{C} \leftrightarrow [\text{C}^+ : \text{C}^- + \text{C}^- : \text{C}^+]$, i.e. the resonance energy arising from mixing of the purely covalent component of the bond with its ionic components. At the same time, the covalent part alone $\text{C}\cdot\text{---}\cdot\text{C}$, involving singlet-coupling between the two HAOs, although being significantly stabilizing, cannot by itself overcome the large repulsions from the surrounding wing C-C bonds, and is thus overall only slightly repulsive. Such bonds that are dominated by the resonance energy of the constituent VB structures that differ by a shift of charge are qualified as “Charge-shift bonds“ (CSBs) and constitute a bonding class on their own, quite different by many aspects from classical covalent bonds.^[8]

By contrast to the BOVB study, the bridgehead bond was diagnosed as being absent in the LCFVC paper, on account that the negative $\Sigma(\text{DOF}_i)$ of the MOs considered as being relevant to this bond (we will come back to this point later). Since the correlations of $\Sigma(\text{DOF}_i)$ to bonding energies (BEs) were established for a series of CC bonds that are all of classical covalent bonding types,^[7] whereas the bridgehead bond of [1.1.1]propellane was characterized as a typical CSB by our high level *ab initio* valence bond study, it is therefore important to check whether or not the DOF-BE relationship still holds for CSBs. Furthermore, since CSBs

are generally found when the bond is surrounded by adjacent Pauli repulsion, it is also useful to test the adequacy of the DOF method for handling this latter kind of electronic interaction. These two key questions are addressed here by means of our own DOF calculations in the three following sections, in the light of the DOF analysis of the prototypes ground state of difluorine anion F_2^- (which is a pure CSB), and of the excited $^3\Sigma_u$ triplet (which is repulsive and devoid of any bond) and ground $^1\Sigma_g$ states of difluorine F_2 (which is a CSB in the ground state).

Is the DOF method reliable for Charge-shift bonds? The difluorine anion example

The difluorine anion, F_2^- , is a typical example of a two-center three-electron (2c,3e) bond, usually represented as $[F \cdot : F]^-$. In MO terms, such bonds display a doubly occupied bonding MO and a corresponding singly occupied antibonding one. In terms of Lewis structures, $[F \cdot : F]^-$ is a resonating combination of two components, $F^- \cdot F$ and $F \cdot : F^-$. As each of these components is, by itself, dissociative,^[9,10] the totality of the bonding energy arises from the electron fluctuation, i.e. the resonance between the charge-shift related structures $F^- \cdot F \leftrightarrow F \cdot : F^-$. As such, the bond in F_2^- , like all (2c,3e) bonds,^[8,10,11] is a pure CSB. How does the DOF method account for the existence of this bond and its bonding energy?

To address this question, we performed DOF calculations on F_2^- at the Restricted Open-Shell Hartree-Fock level (ROHF), using a quadruple-zeta Dunning basis set, aug-cc-pVQZ, with an interatomic distance optimized at the CCSD(T)/aug-cc-pVQZ level. The Gaussian 09 program was used throughout.^[12] The results are displayed in Table 1.

Table 1. Energy derivatives of valence MOs of F_2^- in its $^2\Sigma_u$ anionic state, and of F_2 in its $^3\Sigma_u$ triplet and $^1\Sigma_g$ ground states, as calculated at the Hartree-Fock and density functional levels, in aug-cc-pVQZ basis set. The F-F interatomic distance in F_2 is 1.412 Å, and 1.9202 Å in F_2^- . The Σ DOF values are calculated by summing up the DOFs of the orbitals multiplied by their respective occupancies.

MOs	$^2\Sigma_u F_2^-$ ROHF	$^2\Sigma_u F_2^-$ UBHandHLYP		$^3\Sigma_u F_2$ ROHF	$^1\Sigma_g F_2$ HF
	DOF	DOF alpha	DOF beta	DOF	DOF
$1\sigma_g$	0.021	0.016	0.019	0.241	0.262
$1\sigma_u$	-0.066	-0.050	-0.048	-0.159	-0.140
$1\pi_u$	-0.003	-0.003	0.000	0.108	0.108
$1\pi_g$	-0.058	-0.040	-0.040	-0.095	-0.103
$2\sigma_g$	0.066	0.024	0.042	0.090	0.198
$2\sigma_u$	-0.090	-0.09		-0.238	
Σ DOF (σ)	-0.048	-0.087		0.016	0.640
Σ DOF (π)	-0.243	-0.164		0.053	0.021
Σ DOF (total)	-0.291	-0.251		0.069	0.661

At the ROHF level, F_2^- possesses the configuration $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 1\pi_g^4 2\sigma_g^2 2\sigma_u^1$ (dropping the core MOs). It may first be noted that the DOFs correctly characterize the bonding/antibonding natures of the MOs (if one excepts the $1\pi_u$ MO which is found non-bonding), in agreement with the early aims^[6] of this method: the $1\sigma_g$ and $2\sigma_g$ MOs are found to be bonding, all with positive DOFs, whereas $1\sigma_u$, $1\pi_g$ and $2\sigma_u$ have negative DOFs, hence antibonding. However, the sum of the DOFs over all occupied MOs, ΣDOF_i , is significantly *negative*, (-0.291 a.u.), *hence predicting the absence of any bond between the two atoms, and that F_2^- would be dissociative*. This is of course in absolute disagreement with the experimental bonding energy of F_2^- , 30.2 kcal mol⁻¹.^[13]

It is noteworthy that the BOVB method, the same as the one that characterized the σ bridgehead bond of [1.1.1]propellane and whose results are challenged in Ref. 1, yields a bonding energy of 30.4 kcal mol⁻¹ for F_2^- ,^[10] in perfect agreement with experiment.

To check the effect of changing the Hartree-Fock MOs to Kohn-Sham MOs, as done in Ref. 1, and argued to tentatively bring in electron correlation, we restarted the DOF calculations by using the density functional that was shown to yield the best (2c,3e) bonding energies,^[14] the BHandHLYP functional, in the spin-unrestricted version to maximize accuracy. The results are displayed in Table 1, and are quite similar to the ROHF results, with a negative ΣDOF_i of -0.251 a.u., hence still predicting a dissociative F_2^- anion. Note that even if ΣDOF_i is restricted to the valence MOs of σ type only (those directly responsible for the 2c-3e bond), the value is found to be substantially negative. Thus, in view of these definite failures, one cannot avoid the conclusion that the ΣDOF_i method, when used as means of predicting the existence or absence of bonds actually fails to do so when the bonds are CSB types. But this is not the only failure...

Does the DOF method handle Pauli repulsion? The $^3\Sigma_u$ triplet state of F_2 .

In the MO framework, the ground configuration of the $^3\Sigma_u$ state of F_2 is $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 1\pi_g^4 2\sigma_g^1 2\sigma_u^1$. The elementary representations of this state are equivalent in the Hartree-Fock and valence bond frameworks, and in the latter the picture is that of two fluorine atoms displaying some Pauli repulsion between their respective σ HAOs, each bearing a single electron with alpha spin. In accord, at the F...F distance of 1.412 Å (the equilibrium distance of singlet F_2) the $^3\Sigma_u$ state of F_2 lies some 110 kcal mol⁻¹ above the two separate $F\bullet$ atoms, as calculated at the ROHF level.

The results of our DOF calculations on the ROHF wave function of the $^3\Sigma_u$ state at an

interatomic distance of 1.412 Å are displayed in Table 1. Once again, the bonding/antibonding characters of the MOs are correctly assigned by the respective DOFs, positive for the bonding orbitals and negative for the antibonding ones. On the other hand, the strongly repulsive nature of this triplet state is definitely missed by the sum of the DOFs over all the occupied orbitals, as ΣDOF_i is found to be slightly *positive* (0.069), which in this framework would characterize a slightly attractive interaction.

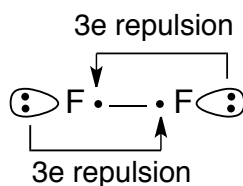
Furthermore, this ΣDOF_i value can be decomposed into an interaction ($\Sigma\text{DOF}_{i,\sigma} = 0.016$) that is close to non-bonding in the σ system, despite the expected repulsion between two electrons with parallel spins, and a slightly attractive interaction in both π systems ($\Sigma\text{DOF}_{i,\pi} = 0.053$). These assignments are in contrast with the fact that each of these DOF components is a closed-shell system of π lone pairs which should undergo some four-electron-two-orbital Pauli repulsion. So, somehow surprisingly, the errors of the ΣDOF_i predictions are in opposite directions for the bonded F_2^- vs. the repulsive triplet state of F_2 . *While in the first case ΣDOF_i predicts a repulsion where there is a bond, in the second case it predicts a slight attraction where there is a strong repulsion.*

The ground state of F_2

In view of the above results, it is difficult to tell what would the DOF method predict for the F_2 bond, which is a CSB. On the one hand, this molecule is found repulsive at the Hartree-Fock level (by ca. 31 kcal mol⁻¹ at the experimental bonding distance), so in all rigor the DOF method should find it repulsive too, since it analyzes precisely the Hartree-Fock wave function. On the other hand, F_2 is experimentally found to be bound by 38.3 kcal mol⁻¹.^[15] Be it as it may, the DOF method finds F_2 to possess a large positive ΣDOF_i value (Table 1), and hence to be bound, despite its repulsive nature in the Hartree-Fock level. This latter result deserves comments.

First, the F_2 bond is the site of a strong “lone pair bond weakening effect“ (LPBWE) discovered long ago by Sanderson.^[16] This effect originates primarily in the Pauli repulsion between the bonding electrons and the lone pairs that have the same symmetry as the bond, as shown in Scheme 2, and was estimated as ca. 77 kcal mol⁻¹ in a computational study.^[17] Second, the charge-shift resonance energy (RECS) arising from the mixing of covalent and ionic structures is also very large, computed as 67 kcal mol⁻¹, making this molecule the prototype of pure CSB.^[18] As was seen above, the neglect of these two effects by the DOF method is responsible for the DOF failure in triplet F_2 , as well as for the failure in F_2^- . On the

other hand, since the LPBWE and RE_{CS} are respectively repulsive and attractive, their joint absence in the DOF analysis of F_2 somehow cancel out, so that the DOF result is correct, owing to cancellation of errors.



Scheme 2. The LPBWE in the ground state of F_2

Interestingly, the ΣDOF_i value for F_2 is quite large, 0.661 a.u. and even 0.826 a.u. in Ref. 7, to be compared with 0.412 a.u. for ethane,^[7] whereas the bond strengths (D_e values) are in the reverse order, 38.3 and 97.0 kcal mol⁻¹, respectively.^[15] This apparent paradox can be explained by the fact that the DOF method is based on orbital-energy derivatives, while orbital energies are themselves dominated by the reduced resonance integral β for bonding as well as antibonding MOs. Therefore, the DOF for a given MO is directly connected to the variation of β with the interatomic distance. However, all other things being equal, this β integral increases in absolute value from left to right of the Periodic Table^[18] and so does its derivative, thus explaining the large ΣDOF_i value found for F_2 , entirely based on a counting of orbital energy derivatives, but not quantifying the strength of the respective bond.

DOF Analysis of the inverted bond in [1.1.1]propellane

The β -dependence of the DOF method has an interesting consequence. Apart from the above-noted tendency in the Periodic Table, the β integral is proportional to the overlap between the fragments that are involved in the bond. Now, because in such cases the hybrid atomic orbitals (HAOs) interact by their smaller lobes, this overlap is inevitably close to zero in the case of inverted bonds and is not expected to vary significantly with the carbon-carbon distance, leading to a quasi-zero β integral derivative. It follows that the DOF method is, in principle, unable to detect an inverted bond, be it in [1.1.1]propellane or anywhere else.

Another problem with the DOF analysis of [1.1.1]propellane is that it cannot cleanly separate the wing bonds from the central bridgehead bond in the canonical MOs representation, due to the fundamentally delocalized nature of these MOs. In Ref. 1, the MOs are divided into two categories, π (e' and e'') and σ (a'_1 and a''_2), and all the MOs of the latter category are arbitrarily associated to the central bond, whereas two of these MOs, $9a''_2$ and $13a'_1$, are in fact mixtures of wing and central bonds. In particular, the $9a''_2$ MO should rather

be considered as a negative combination of bonding fragment orbitals localized on wing bonds, as indicated by its shape, the absence of axial p atomic orbitals, and the low orbital energy (-0.533 hartrees, this work). Thus, the largely negative DOF of -0.109 a.u. for this MO is better interpreted as being due to the out-of-phase combination of bonding wing orbitals rather than to the minor contribution of the central bond. Now, keeping or removing this MO from the DOF analysis reverses conclusions of the analysis, which leads to a very small but positive DOF value, in accordance with the very small β in this case. In view of such uncertainties, the attribution of a ΣDOF_i of -0.029 a.u. to the central bridgehead bond alone appears as largely arbitrary. Incidentally, this difficulty to separate interactions from each other is also the problem that is encountered in the first section of the LCFVC paper, with the inverted C_2H_6 model. As the two methyl fragments approach each other in an inverted geometry, some H-H repulsions take place, blocking the approach at a long distance and preventing any CC bond formation.

However, this latter issue with the DOF analysis, which surfaces in systems that are more complex than simple diatomic molecules, is secondary. The main problems of DOF in analyzing the inverted bond in [1,1,1]propellane, are: i) the inability of the DOF method to account for the “charge-shift” component of bonding as illustrated with F_2^- prototype case, ii) the inability of this method to probe situations of large Pauli repulsion, iii) the DOF’s inability to probe bonding situation occurring when the overlap and thus β resonance integral derivative is small. All these factors combine here in the case of the inverted bond of [1,1,1]propellane: large RE_{CS} has been previously quantified by means of accurate high level *ab initio* valence bond calculations, a large Pauli repulsion is present due to small-rings strain, and a quasi-zero β resonance integral derivative is expected from the quasi-zero overlap between the hybrids involved in the inverted bond.

Conclusion

The DOF method which deals with derivatives of orbital energies may be useful and correlated to bond strengths in cases of small molecules displaying classical covalent bonds, where significant overlap between the respective fragment orbitals of the two atoms is the main factor of bonding, and furthermore if the bonding/antibonding character of MOs is well localized on the bond under study.

For more complex cases, when several factors come into play, the DOF model which is based on sums of MO energy derivatives inevitably misses some important features of the chemical bond, e.g., the Pauli repulsions or charge-shift resonance energies. As a

consequence, the DOF method may fail to find bonding interactions, where there is repulsion, and repulsive interactions, where there is a significant bond. This was demonstrated in the case of difluorine in its triplet and anionic states. Finally, switching from Hartree-Fock MOs to Kohn-Sham orbitals as suggested in Ref. 1 does not improve the predictive accuracy of DOF, as shown in the F_2^- example.

These severe failures, as well as the delocalized character of the MOs where wing bonds and the central bond are entangled, make the DOF method an inappropriate tool for characterizing the CC inverted bond in [1.1.1]propellane, which is revealed by direct *ab initio* valence bond calculations^[5] as well as electronic stress tensor analysis,^[19] density decomposition into paired and unpaired contributions,^[20] and experimental Laplacian of the bond critical point.^[21]

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