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Electron-pair bonding in real space. Is the charge-shift family supported?

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Charge-shift bonding (CSB) has been introduced as a distinct third family of electron-pair links that adds to the covalent and ionic tradition. However, the full battery of orbital invariant tools provided by modern real space artillery shows that it is difficult to find CSB signatures outside the original valence-bond framework in which CSB was developed. The CSB concept should therefore be further investigated.

More than a hundred years after Lewis seminal paper,¹ the electron-pair bond may still be considered the most central concept in Chemistry. After its inception, its initial theoretical development by Heitler-London² and its incorporation to mainstream computational chemistry,³ the Lewis pair lies at the core of chemical thinking. Through Pauling's⁴ tour de force, the shared electron pair gave rise to the two major covalent (or polar-covalent) and ionic bonding families. These emerge as the degree of atomic sharing of the pair deviates from equality, and have carved the chemists' way of thinking. Subjected to reasonable generalizations, the covalent-ionic dichotomy has resisted exceedingly well the test of time.

Fundamental as they are, neither the Lewis pair nor the electron-pair bonding families are linked to quantum mechanical observables, and their significance rests on how a provided quantum mechanical wavefunction Ψ is interpreted. Usually, this relies on what theoretical framework has been used to generate Ψ , and although as the level of theory is improved all frameworks converge, interpretations do not necessarily do so, *vanishing into thin air*.⁵ To understand how an electron pair is shared between two atoms, we have to deal with at least (i) the indistinguishability of electrons and electron pairs and (ii) the absence of isolatable atoms in the quantum mechanical description of two interacting systems. How this is done depends on the theoretical paradigm used, e.g. the valence bond (VB) or the molecular orbital (MO) viewpoints.

The existence of two main pair-electron bonding families has been challenged by the addition of a new *charge-shift bonding* (CSB) category. This is introduced in non-orthogonal VB (NOVB)

as a distinct bonding class in which the bonding energy does come neither from the so-called spin-pairing of covalent bonds nor from the electrostatic stabilization of ionic links, but from the large resonance energy (RE) between the VB covalent and ionic structures. Although the paradigm of a CSB system is the F_2 molecule, whose VB covalent structure is unbound in marked contrast to a *normal* covalent bond like the one in H_2 , many other cases have been found over the years, and a number of informative presentations can be found in the literature.⁶

Since according to Carl Sagan's standard, *extraordinary claims require extraordinary evidence*, the proposers of the CSB category have tried to offer that evidence by linking CSB to MO theory; to real space descriptors of chemical bonding like density differences, the laplacian of the electron density or the electron localization function (ELF); and to experimental behavior. Charge-shift bonds were soon associated to systems affected by the lone pair bond weakening effect (LPBWE) described by Sanderson,⁷ so efforts have also been put on rationalizing their physical origin.⁸ This was found to lie in very large kinetic energies coming from two-center three-electron Pauli repulsions between bonding electrons and compact lone pairs.

A decisive test of any new concept should be its independency from the theory used to *discover* or define it. In chemical bonding a framework invariant paradigm is available. It is based on (i) partitioning the space into 3D regions associated to atoms and (ii) on computing quantum mechanical observables within these regions. Although several partitioning strategies exist, the one provided by the quantum theory of atoms in molecules (QTAIM) is widely used.⁹ These techniques need only a proper wavefunction, are orbital invariant by construction, and provide indices and energetic quantities which are directly related to Lewis' concepts.

In this Communication we show that charge-shift bonds display all the characteristics of a standard covalent interaction at larger

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than expected distances. The latter are forced by the LPBWE, but the nature of the interaction has no specific peculiarity. This is found by critically examining the CSB family in the light of real space reasoning.

Electron-pair bonding in real space

Real space theories of the chemical bond have acquired a considerable level of maturity and notoriety.¹⁰ Once an atomic partition of space is defined appropriately (through the QTAIM, for instance), one has access to both electron counting (through electron distribution functions, EDFs¹¹) and energetic (through the interacting quantum atoms scheme, IQA¹²) descriptors. EDFs, that provide the probability of finding a given distribution of the N electrons of a system into atoms, behave as Pauling's resonance structures. Their knowledge gives also the average atomic electron population (thus the atomic net charge, Q^A and the ionic bond order,¹³ $\iota^{AB} = -Q^A Q^B$) and all their further statistical moments. The interatomic covariance, or an equivalent form known as the delocalization index δ^{AB} , measures the number of shared electron pairs between atoms and provides the covalent bond order.¹⁴ Similarly, the binding energy of a molecule becomes a sum of atomic deformation energies, E_{def}^A , and interatomic interactions, E_{int}^{AB} . The former basically correspond to traditional promotion costs, and the latter determine *in situ* bond energies, separated into covalent (cov) and electrostatic (ion) terms. For each atomic pair, the covalent energy is proportional to the number of shared pairs, while the electrostatic one is dominated by the product of the atomic charges. Ionicity and covalency are thus uniquely and invariantly defined. A brief introduction to this formalism is found in the supplementary information (ESI).

For two-center (A,B) electron-pair bonds, only three electron distributions are possible. Two zwitterionic, with the two electrons residing on either of the atoms $-(2, 0)$ and $(0, 2)$ —, and one similar to the VB-covalent structure, $(1, 1)$. Denoting the probability that one electron lies in A as p and using a $-1 \leq f \leq 1$ correlation factor between the two electrons, all 2c,2e links can be mapped. It is easy to show (see the ESI) that $\iota + \delta = 1$ when $f = 0$, so that ionicity excludes covalency and vice versa for electron-pair links (not in more complex situations¹⁵), and that $\delta = 4p(1-p)(1-f)$, this meaning also that covalency comes from electron delocalization and that it implies a non-vanishing population of the real space ionic resonance structures. A full classification for correlated situations is also known.¹⁶

Charge-shift bonding

CSB in NOVB appears when much (or all) of the binding energy of a system comes from the resonance energy between the VB-covalent, Ψ_{cov} , and the VB-ionic, Ψ_{ion} , structures, i.e. when neither $\langle \Psi_{cov} | \hat{H} | \Psi_{cov} \rangle$ nor $\langle \Psi_{ion} | \hat{H} | \Psi_{ion} \rangle$ is appropriately bound and it is $\langle \Psi_{cov} | \hat{H} | \Psi_{ion} \rangle$ that determines the bond energetics. Being consubstantial to Quantum Mechanics via the superposition principle, resonance is representation dependent: a change of basis changes its value. Even more, two non-orthogonal states coupled by a large resonance integral may become uncoupled after orthogonalization, and vice versa. *The resonance energy condition is therefore not invariant, and cannot serve our purpose to uncover*

invariant features of CSB. Arguments based on two-configuration self-consistent field calculations,¹⁷ that have been offered as a proof that CSB also appears under MO theory, simply mimic the NOVB wavefunction, and do not change the above conclusion. In the form of a two-electron two-orbital configuration mixing (CI(2,2)), this oversimplified description captures the essential elements of CSB, allowing us to examine it also under a real space perspective. To that end, we construct a model homoatomic two-electron wavefunction with strictly localized functions a and b with overlap $\langle a|b \rangle = S$, so that the g and u orthogonal MOs are written as $g, u = N_{g,u}(a \pm b)$. The spatial parts of the Heitler-London VB singlet covalent and ionic functions are the textbook $\Psi_{cov} \equiv (ab + ba)$ and $\Psi_{ion} \equiv (aa + bb)$, so that the NOVB function is $\Psi = c\Psi_{cov} + i\Psi_{ion}$, while its complete active space (CAS) analogue becomes $\Psi = \lambda|g\bar{g}\rangle + \mu|u\bar{u}\rangle$, with $\lambda^2 + \mu^2 = 1$. A one-to-one map $(c, i) \leftrightarrow (\lambda, \mu)$ exists. Full details are found in the ESI. The Hartree-Fock mean-field solution corresponds to $\lambda = 1$. In H_2 , Ψ_{cov} provides a rather accurate binding curve, and mixing it with Ψ_{ion} introduces a slight resonance stabilization with a final small i contribution. In F_2 none of Ψ_{cov} , Ψ_{ion} or Ψ_{HF} are bound, but the CAS(2,2) Ψ is. Such a calculation within the $2p_z$ manifold with a 6-31G* basis provides $R_e = 1.48 \text{ \AA}$ and $D_e \approx 16 \text{ kcal mol}^{-1}$, to be compared with the experimental 1.40 \AA and 39 kcal mol^{-1} values, respectively. The essential features of CSB are thus captured by this naive model. If orbitals are not allowed to relax, then the Ψ_{cov} and Ψ_{ion} functions correspond to a $(\lambda_c, -\mu_c)$, (λ_c, μ_c) pair, with $\lambda_c, \mu_c > 0$, respectively. Ψ_{HF} lies at $\mu = 0$, so examining the $-\lambda_c \leq \mu \leq \lambda_c$ window provides a continuous map that visits all the four Ψ_{cov} , Ψ_{CI} , Ψ_{HF} , and Ψ_{ion} states. We use CAS orbitals in the following. It is relevant (ESI) that the first and second order densities of the 2e subsystem have very simple expressions in the λ, μ space: $\rho(\mathbf{r}; \mathbf{r}') = 2\lambda^2 g(\mathbf{r})g(\mathbf{r}') + 2\mu^2 u(\mathbf{r})u(\mathbf{r}')$, so any one-electron operator property varies linearly with λ^2 ; $\rho_2(\mathbf{r}_1, \mathbf{r}_2) = 2\lambda^2 g^2(\mathbf{r}_1)g^2(\mathbf{r}_2) + 2\mu^2 u^2(\mathbf{r}_1)u^2(\mathbf{r}_2) + 2\lambda\mu g(\mathbf{r}_1)u(\mathbf{r}_1)g(\mathbf{r}_2)u(\mathbf{r}_2)$. The latter expression shows that the $gg - uu$ resonance lies only in the two-electron $2\lambda\mu g(\mathbf{r}_1)u(\mathbf{r}_1)g(\mathbf{r}_2)u(\mathbf{r}_2)$ term if orbitals are not relaxed. This points to electron-electron repulsion, and not to the large kinetic energy of the covalent term (as usually admitted in the CSB literature) as the driving force for CSB.

Plenty of real space signatures of CSB have been reported so far.¹⁸ For instance, negative deformation electron densities between the nuclei, indicative of density retraction in the bonding region. However, as recognized,¹⁸ $\Delta\rho$ is reference dependent, and a change from spherically-averaged to valence-prepared atomic references may change the sign of $\Delta\rho$, which is not invariant. The sign of the laplacian of the density at the QTAIM bond critical point (bcp) has also been advocated as a CSB feature. A homonuclear covalent system usually displays $\nabla^2\rho(\mathbf{r}_{bcp}) < 0$ values, but these become positive in F_2 and many other CSB cases. Recall, however, that for a simple $\rho(r) = Ne^{-\zeta r}$ exponential decay $\nabla^2\rho(r) = Ne^{-\zeta r}(\zeta^2 - 2\zeta/r)$, that turns positive after a critical distance. For instance, when stretching a normal H_2 molecule, its laplacian becomes positive at the bcp at about $R_{HH} = 3.2 \text{ au}$, so that a positive laplacian just indicates a too long distance. Moreover, since in a homodiatomic $u(\mathbf{r}_{bcp}) = 0$, it can be shown (ESI) that $\nabla^2\rho(\mathbf{r}_{bcp})$ is positive if $\mu = 1$, so a large g, u mixing makes

Table 1 6-31G* data for F₂ with CAS(2,2) orbitals at R_e = 1.49 Å. gg and uu refer to MO determinants built from fixed CAS orbitals. The CAS contributions have been separated into those of the 2e active system and those of the remaining 16e electrons. The latter are also classified into π and σ symmetries. All data in au obtained at the bcp.

Ψ	ρ _{bcp}	∇ ² ρ	ELF	CAS		
				18e	ρ _{bcp}	∇ ² ρ
gg	0.22	0.46	0.57	16e	0.06	0.90
CAS	0.21	0.66	0.43	2e	0.15	-0.23
uu	0.06	2.68	0.02	π	0.00	0.42
				σ	0.06	0.48

the laplacian tend to a positive value necessarily, whatever the distance. Similarly, g, u mixing decreases ρ(r_{bcp}) from g²(r_{bcp}) to 0 as λ goes from one to zero (ESI). Since all these properties depend on the one-matrix, and we have just shown that resonance is a two-electron phenomenon in an orthogonal framework, neither the behavior of the density nor of the laplacian can be related to covalent-ionic resonance in CSB.

The results of this model can be tested on real calculations. Table 1 shows how scalar fields at the bcp behave in F₂. Interestingly, ρ is dominated by the 2e active subsystem, but ∇²ρ is not. Surprisingly, ∇²ρ of the 2e subsystem is negative, like in H₂, and it is the effect of the *non-bonding* electrons that makes it overall positive. A similar criticism can be cast on arguments based on the ELF function, which is commonly obtained from the 1-matrix. CSB has been related to small ELF bonding domains with low electron count and large population variances (or fluctuations). However, the standard ELF function is difficult to generalize outside the single-determinant (SD) framework¹⁹ (needed to deal with CSB), shedding doubts on its meaning. Moreover, variances obtained from SD expressions are in gross error when applied to correlated (or DFT) descriptions. Sometimes, even the ELF disynaptic bonding domain is absent in high accuracy wavefunctions (like in coupled-cluster calculations of F₂¹⁸) and the variance argument can simply not be applied. All this is compatible with an old proposition that would consider F₂ and other systems in a proto-bonding situation,²⁰ but is hardly related with covalent-ionic resonance.

Turning to cohesion, CSB has been linked to the kinetic energy (T), in line with Kutzelnigg and Ruedenberg classical arguments,²¹ although the latter have been criticized for they ignore other equally important energy components in favor of T.²² According to this view, in standard covalent bonding the virial theorem is restored as a bond is being formed through an increase in T driven by orbital contraction. When lone pairs give rise to large T's due to 2c-3e repulsions, a new restoration mechanism sets in and heavy mixing with the ionic configurations, which largely decrease T, serve this purpose. As a result, *large fluctuations of the pair density are thought to appear*.¹⁸ However, in a fixed orbital framework which allows comparison across VB or MO paradigms, T, a one-electron property, changes linearly (with λ²) between its gg (lower) and uu (higher) limits. Were it not for the V_{ee} electron repulsion, there would be no gg,uu mixing at all. Moreover, T in the covalent and ionic mixtures (ESI) are identical with fixed orbitals. Table 2 shows actual data. For fixed orbitals, the HF determinant always displays the smallest T, but its density is not

Table 2 Total energy components for several 6-31G* wavefunction of F₂ with fixed CAS(2,2) orbitals at R_e = 1.49 Å. All data in au (198 and 533 au have been added to E and V_{ne} respectively, and 198, 108, and 20 au subtracted from T, V_{ee}, and V_{ee}^{ca}, respectively). Energy at the dissociation limit E = -198.724 au. λ_{cov} ≈ 0.83 estimated from orbital overlaps (ESI). V_{ee}^a and V_{ee}^{ca} are the interelectron repulsion among the active electrons and among the frozen core and the active electrons, respectively.

Ψ	E	T	V _{ne}	V _{ee}	V _{ee} ^{ca}	V _{ee} ^a
gg	-0.656	-0.034	-0.373	0.025	0.264	0.660
CAS	-0.751	0.290	-0.811	0.044	0.444	0.499
cov	-0.641	1.229	-2.078	0.482	0.967	0.414
ion	-0.075	1.229	-2.078	1.048	2.001	0.980
uu	0.173	3.475	-5.110	2.083	2.220	0.762

Table 3 Relevant IQA data in 6-31G* for different two-state wavefunctions of H₂ and F₂. λ_{cov} ≈ 0.982 in dihydrogen. All data in au and all orbitals and distances fixed to those in the CAS.

H ₂	E _{def} ^A	T ^A	V _{ee} ^{AA}	E _{int} ^{AB}	E _{cov} ^{AB}	V _{ee} ^{AB}	δ ^{AB}
cov	0.005	0.601	0.136	-0.153	-0.194	0.321	0.715
CAS	0.013	0.578	0.165	-0.189	-0.222	0.296	0.833
HF	0.043	0.567	0.198	-0.230	-0.262	0.269	1.000
ion	0.132	0.601	0.263	-0.280	-0.321	0.195	1.284
F ₂	E _{def} ^A	T ^A	V _{ee} ^{AA}	E _{int} ^{AB}	E _{cov} ^{AB}	V _{ee} ^{AB}	δ ^{AB}
cov	0.092	99.614	40.435	-0.084	-0.122	27.611	0.397
CAS	0.077	99.145	40.237	-0.164	-0.199	27.569	0.713
HF	0.173	98.983	40.270	-0.263	-0.297	27.484	1.206
ion	0.526	99.614	40.870	-0.387	-0.425	27.381	2.040

compact enough and the total one-electron energy (T + V_{ne}) is more stabilizing for the uu state than for the gg one (contrarily to what happens in H₂, see the ESI). From the VB point of view, the covalent structure has too large T, and the system responds by c, i mixing so that both T and the electron repulsion decrease.

A clue about the effect of c, i or λ, μ mixing is found on separating V_{ee} into core-core (c), core-active (ca) and active-active (a) pieces. The former is constant, the latter is smallest in the Ψ_{cov} calculation (as in H₂ with no lone-pairs). It is thus the ca repulsion that dominates the global V_{ee} behavior, being too large in the VB covalent structure. *The absence of lone pairs leads to no V_{ee}^{ca}, to a one-electron energy decreasing from uu to gg, and to small c, i mixing that decreases V_{ee} of the active orbitals. The presence of many lone pairs leads to the contrary behavior: one-electron energy decreasing towards uu, dominating ca repulsion, and large c, i mixing that tries to decrease its impact.* As shown in the ESI, the first behavior is found from H₂ up to N₂, the second in O₂ and F₂.

Is then CSB a distinct family of pair-electron bonding? Real space analysis clarifies this by answering the following questions: Is covalency changed in any substantial way in CSB? Is CSB characterized by a larger than usual fluctuation of the electron pair? IQA data for the model 6-31G* H₂ and F₂ systems are found in Table 3. Notice that in homodiatomics, all real space partitions coincide with that of the QTAIM. As seen, the covalent interaction in both CAS models as well as their delocalization indices are quite similar. In H₂, as expected, atomic deformations grow from the covalent to the CAS to the ionic solutions as we increase the contribution of the deformed hydride-like terms. The optimal CAS mixing is achieved close to Ψ_{cov}: the slight increase in the CAS E_{def} is compensated through E_{int} via E_{cov}. In F₂, E_{def}(Ψ_{cov}) is almost 20 times larger than in H₂, with a rather smaller E_{int}

(due to a larger distance and a more compact electron distribution). Mixing increases the interaction, as in H_2 , but decreases the deformation. Going further, *this is clearly due to a considerable decrease in the intra-atomic electron repulsion, which is minimum in the CAS function*. As shown in the ESI, the larger than expected distance is a direct effect of this intra-atomic effect, which grows very quickly on approaching the two atoms. Aside from this, covalency displays the standard behavior overall. Invariant real space arguments uncover intra-atomic electron repulsion as the driving force behind CSB anomalies. *These are carried over with the atom, in agreement with Sanderson's LPBWE insights*. As fluctuations are regarded, the EDF shows only one delocalized electron pair in F_2 , so only the (9,9) and (10,8) \equiv (8,10) structures have non-negligible probabilities. In the CAS solution of H_2 , $p(1,1) = 0.583$, $p(2,0) = 0.208$. At the CAS solution of F_2 , no anomalous fluctuation is found, with $p(9,9) = 0.684$ and $p(10,8) = 0.151$, the latter being even smaller than $p(2,0)$ in H_2 , in line with the similar structure VB weights for H_2 and F_2 (ESI). This is compatible with a proto-bond with hindered delocalization. *At complete variance with CSB arguments, the electron-pair fluctuation is smaller in F_2 than in a purportedly normal covalent bond*.

All these model results, which we think provide useful insights, are fully supported by heat-bath multiconfigurational correlated calculations that match well the experimental bond distances and dissociation energies, both in F_2 and in a number of representative CSB systems. Details are found in the ESI. In F_2 , for instance, a (23,14) AVAS CASSCF provides a much compacted $R_e = 1.41$ Å, but a fluorine deformation energy of 0.078 au very close to that in the model, a stronger covalent energy of -0.259 au, and a considerably smaller electrostatic repulsion that justifies the increased binding. In these higher levels of theory the intra-atomic repulsion is lower and permits a decrease in R_e together with a more extensive delocalization. δ increases to 0.886, although its main σ eigen-component is still low (0.613), and $p(9,9) = 0.609$, $p(10,8) = 0.188$ approach the values of a correlated 2c-2e covalent bond with $f = 0.21$. Equivalent insights are obtained after examining the $Z = 6, 7, 8$ second period diatomics, N_2H_4 , H_2O_2 , heavier representative diatomics like S_2 , Cl_2 , Br_2 , and some CSB transition metal systems like Cu_2 , Ag_2 , Au_2 or Hg_2^{2+} (ESI). Finally, polar CSBs, like those in H-F, C-F, or Si-F bonds have also been analyzed. In CH_3F , for instance, the $CH_3-F -0.393$ au ionic bond energy is considerably larger than the -0.261 au covalent one, with $\delta = 0.896$. Analysis of the CH_3-F EDF gives $p(n_{CH_3} = 8, n_F = 10) = 0.586$, $p(9,9) = 0.300$, $p(10,8) = 0.076$ which describes a polar interaction with small $f = 0.22$, a value very close to that in F_2 . In SiH_3F , the ionic energy escalates to -0.715 au, covalency decreases with $\delta^{Si,F} = 0.591$, and $f \approx 0.60$. No sign of larger than normal ($f < 0$) fluctuations is found. Much on the contrary, in this case the link has clear proto-bonding ($f \gg 0$) signatures. In propellane, the deformation energy of the bridging carbons (b), E_{def}^b , is even smaller than that for non-bridge C's, E_{def}^{nb} , and a bridge proto-bond is found with $E_{cov}^b = -0.109$ au, $\delta^b = 0.410$.

Summarizing, although CSB stands out clearly in NOVB theory, it is difficult to find specific invariant signatures of this purported third electron-pair bond family, which in our opinion is still better

described in terms of a classical Sanderson's intra-atomic LPBWE leading to proto-bonding.

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