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Authors: Sason Shaik, David Danovich, John Morrison Galbraith, Benoit Braida, Wei Wu, and Philippe C. Hiberty

Charge-Shift Bonding: A New and Unique Form of Bonding

Sason Shaik*[a], David Danovich[a], John Morrison Galbraith[b], Benoît Braïda[c], Wei Wu[d],and Philippe C. Hiberty*[e]

Dedicated to Roald Hoffmann, a great mentor

Abstract: Charge-shift bonds (CSB) constitute a new class of bonds different than covalent/polar-covalent and ionic-bonds. Bonding in CSB is not contributed by either the covalent or the ionic structures of the bond, *but rather by the resonance interaction between the structures*. This essay describes the reasons why the CSB family was overlooked by valence-bond pioneers (Textbox 1). It then demonstrates that the unique status of CSBs is not theory-dependent. Thus, Valence-bond (VB), molecular-orbital (MO),[21,22] and Energy-Decomposition-Analysis (EDA)[23], as well as a variety of electron-density theories; Electron-Localization Function (ELF),[27] Quantum Thery of Atoms in Molecules (QTAIM),[24] and Electron-Stress Tensor (EST) approaches;[25,26] all these show the distinction of CSB vis-à-vis covalent and ionic bonds. Furthermore, *the covalent-ionic resonance energy can be quantified from experiment*, and hence *having the same essential status as resonance energies of organic molecules, e.g., benzene*. The essay then demonstrates how a variety of bond types -- dative-bonds, coordinative-bonds, and hypervalent-bonds, including 3-electron-bonds -- are CSBs. Subsequently, some experimental manifestations of CSBs are discussed, including recent experimental articulations of the concept.[78,81,82] The essay ends by arguing that the definition of CSB as a distinct family of bonding fulfills the necessary conditions for making such a claim. *The distinction*

between covalent-bonds and CSBs is thus fundamental, with a potential to bring about a Renaissance in the mental-map of the chemical bond, and to contribute to productive chemical diversity.

Sason Shaik is a Saerree K. and Louis P. Fiedler Professor of Chemistry at the Hebrew University. His main interests are in bonding, chemical reactivity, metalloenzymes, and electric field effects in chemistry. Alongside a variety of computational tools, he uses valence bond theory as a conceptual frame, and has developed a number of new paradigms and concepts using this theory. His main recent awards are the Schrödinger Medal (WATOC 2007); the August-Wilhelm-von-Hofmann-Medal (the German Chemical Society, 2012); Membership in the International Academy of Quantum Molecular Science (2015); and The Gold Medal of the Israel Chemical Society (2017). He also writes essays on history, the chemical bond as the heartland of chemistry, science and friendship, chemistry as a central pillar of human culture, etc.

David Danovich was graduated in physics from Irkutsk State University in Russia in 1982 and obtained his Ph.D. degree in Quantum Chemistry therein 1989 under the guidance of Dr. V.G. Zakrzevski and Prof. V.K. Voronov. He was a postdoctoral fellow with Prof. Y. Apeloig at Technion, Haifa, Israel, from 1990 to 1992. In 1992 he joined the group of Prof. S. Shaik at the Hebrew University, where he is currently a senior computational chemist. His current research interests include theoretical studies of unusual chemical bonding based on Valence Bond theory and high level *ab initio* approaches.

John Morrison Galbraith received his PhD in 1997 from the University of Georgia where he worked with Professor Henry F. Schaefer III. He then held postdoctoral positions with Sason Shaik at the Hebrew University and Weston Thatcher Borden at the University of Washington. In 2001 he joined the faculty at Marist College in Poughkeepsie, NY, USA where he is currently Associate Professor of Chemistry. His research is focused on theoretical descriptions

[a]   Prof. Dr. Sason Shaik, Dr. David Danovich
       Institute of Chemistry, The Hebrew University of Jerusalem,
       9190401 Jerusalem, Israel
       E-mail: sason@yfaat.ch.huji.ac.il
[b]   Prof. John Morrison Galbraith
       Department of Chemistry, Biochemistry and Physics, Marist College,
       3399 North Road, Poughkeepsie, NY 12601, USA
[c]   Prof. Benoit Braida
       Laboratoire de Chimie Theorique, Sorbonne Universite, UMR7616
       CNRS, Paris 75252 France
[d]   Prof. Wei Wu
       State Key Laboratory of Physical Chemistry of Solid Surfaces,
       Fujian Provincial Key Laboratory of Theoretical and Computational
       Chemistry, and Department of Chemistry, Xiamen University,
       Xiamen, Fujian 361005, China
[e]   Prof. Dr. Philippe C. Hiberty
       Laboratoire de Chimie Physique, CNRS UMR8000, Bat. 349,
       Université de Paris-Sud, 91405 Orsay Cédex, France
       E-mail: philippe.hiberty@u-psud.fr

Supporting information for this article is given via a link at the end of the document.

of chemical bonding, and the majority of his co-workers are undergraduate students. With a firm foundation in chemical bonding theory, these students are well equipped to excel in any area of Chemistry.

Benoît Braïda is Maître de Conférences at Sorbonne Université, Paris. His research work focuses on chemical bonding. It features developments related to Valence Bond (VB) theory, coupled Quantum Monte Carlo and VB methods, and a real-space interpretative method based on probabilities ; and their applications to the understanding of two-center three-electron bonds, hypervalency, unusual bonding, excited states and reactivity. He has also (co-)organized several conferences, workshops and tutorials in this area.
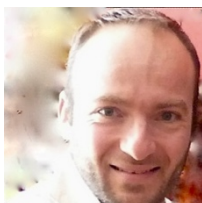
Wei Wu is a Changjiang Scholar Chair Professor at Xiamen University, China. His interests focus on electronic structure theory, especially *ab initio* valence bond theory, including algorithms and methods, software implementations, and applications. He has published more than 180 articles in peer reviewed journals and 5 chapters in monographs.

Philippe C. Hiberty studied theory at the University of Paris-Sud with Prof. W. J. Hehre, and completed his PhD under the supervision of Prof. L. Salem. After postdocs with Profs. J. I. Brauman at Stanford University and H. F. Schaefer III at Berkeley, he went back to Paris-Sud, where he developed a research program based on valence bond theory and on the development of accurate valence bond ab initio methods. He became Directeur de Recherche in 1986, and taught Quantum Chemistry at the Ecole Polytechnique Graduate School in Palaiseau from 1996 to 2007. He received the Grand Prix Philippe A. Guye from the French Academy of Sciences in 2002. His research interests, among others, are in the application of quantum chemistry and valence bond theory to fundamental concepts of organic chemistry.

1. Introduction- The Bond: A Heartland of Chemsitry[1]

The current classification of electron-pair bonds into "covalent (polar-covalent) and ionic families" has empirical foundations,[1-4] rooted in the emergence of inorganic and organic chemistries as distinct sub-branches in the second half of the 19th century. This development made chemical epistemology ripe for articulating a "theory of union between atoms".[2-4] Thus, on the one hand, the advent of electrochemistry had revealed negative and positive species as building blocks of inorganic compounds.[3b] The presence of such ions in strong electrolytes was deduced in due course from conductivity (in solution and molten phases) and colligative properties (osmotic pressure, boiling point, freezing point), which showed e.g., in NaCl, that the number of particles in the solution is doubled vis-à-vis the stoichiometric formula. On the other hand, organic chemistry flourished using structural concepts devoid of ions. These fundamentally different behaviors implied different types of unions between atoms or fragments in compounds belonging to these two chemical sub-fields.

Indeed, the ubiquity of ions among inorganic compounds, led initially to the formulation of the "dualistic electric theory" of bonding by Berzelius and Davy.[2,3a] This theory postulated the existence of union due to attractions between oppositely charged ions. At the same time, organic chemists explored the ideas of "valence" and "structure"[5] and had no use for ionicity, and hence, they dismissed the ionic theory. As such, a unified theory of union was in need in order to bridge these very diametrically different concepts. [4b-d;5,6]

On this background, the electron was discovered and characterized by J. J. Thomson as a source of negative electricity. Subsequently, the inner structure of the atom was revealed by Rutherford to involve a positively-charged nucleus "surrounded" by electrons. The ionic bonding was soon revived by Thomson.[7,8] However, since the notion of oppositely charged ions could not account for the nonpolar (nonionic) organic substances or for their respective structures, ionic theories were deemed unsuitable as general formulations of chemical-union. At the same time, the structuralists (like Frankland, Kekulé, Couper, Butlerov, Laurent, Gerhardt, Cannizzaro, Wurtz, ...) emphasized the concept of "structure" of organic compounds[4b,d] that could be deduced directly from atomic valences, which were determined as the ratios of the respective atomic weights to the combining weights, and were articulated as coordination spheres of the atoms, and groups of atoms that appeared as Lego pieces (so-called "radicals") in many compounds.

This dichotomy of *two types of chemical compounds* was a call for generalization, which needed a hero who would 'pick up the gauntlet' and meet the challenge. This person was Gilbert Newton Lewis, who articulated these differences in a unified manner. Already in 1913,[6] Lewis wrote: "…*the 'valence' theory, which is the classical basis of structural organic chemistry, deals with the fundamental structure of the molecule, while the electrochemical considerations show the influence of positive and negative groups*…".

Subsequently, in his pioneering 1916 paper[9] Lewis formulated the union between atoms/fragments as an *electron-pair bond*, which was shared in organic compound between the constituent fragments (later to be named 'covalent' bonding by Langmuir[10,11a,b]) while in inorganic ones, the pair was appropriated by the more electronegative fragment/atom in an

ionic bond. On page 782 of his paper, he stated: "*… I believe enough has been said to show how, through simple hypotheses, we may explain the most diverse types of chemical union and how we may construct models which illustrate the continuous transition between the most polar and the most nonpolar of substances*".

Thus the electron-pair bond was formulated in 1916, in a time where the physics community was still wondering how could two neutral species make a bond (a 1923 letter of Born to Einstein[11c]). The role of theory reached only a decade later. Within the years 1927-1928, the new theory of quantum mechanics provided a physical basis for the electron-sharing idea, through the pioneering work of Heitler and London (HL)[12] and the subsequent generalization by London.[13] During the years 1931-1950s, Linus Pauling and John Slater extended the new theory to a variety of molecules from the simplest diatomic molecules all the way to polyatomic ones. This theory has become known as valence-bond (VB) theory. [14,15]

Pauling described the electron-pair bond as a superposition of covalent- and ionic-structures, and devised empirical ways for calculating the VB wave function and bond energy.[14a,c] Using auxiliary empirical data of bond energies, he quantified the electronegativity scale,[14a-c;16] and *showed how bond-polarity emerged from electronegativity differences between the two atoms/fragments in union.*

Pauling's VB approach revealed practically two bonding families, the covalent-(plus polar-covalent)-bonds and the ionic-bonds. This was essentially a theoretical articulation of the Lewis model,[4c] which had been deduced empirically 15 years before. As such, the classification of electron-pair bonding is now over 100 years old, and its foundations are basically empirical, albeit dressed with VB wave functions or molecular orbitals.

Despite the great progress in computational chemistry in molecular-orbital (MO)-based theories[17] and density functional theory (DFT), this classification has stood the test of time and it remains useful to-date. Nevertheless, in the course of time, chemists formulated some additional phenomenological bonding types such as "dative bonds" and "coordinative bonds",[11b, 18,19] which may basically fall into the covalent-ionic categorizations.[19c;20] At this point, decades after the foundation of the covalent/polar-covalent and ionic bonding types, it is appropriate to ask: "*is this a complete story of electron-pair bonding*?"

As this essay demonstrates, because *ab initio* VB calculations were not available during the time Pauling developed his bonding ideas, he used approximations. One of these approximations caused *the complete unawareness* of a family of bonds *the charge-shift bond (CSB)-family*. As such, this essay

deals with this new bonding-form that is supported by both VB and MO-based theories,[21,22] as well as by a recent energy decomposition analysis (EDA) scheme of Head-Gordon et al.[23] CSB is further categorized independently by electron density theories (QTAIM,[24] electron density tensor theory[25,26] and ELF[27,28]), and supported by experimental data. The CSB family is wide-ranging involving homonuclear and heteronuclear bonds, of σ and π types, as well as dative, coordinative and hypervalent bonds.

2. How did Pauling's Covalent-Ionic Superposition Approach Miss the CSB Family?

Figure 1 depicts the essential elements for discussing the electron-pair bonding using VB theory. Figure 1a displays the three VB structures needed for the description of an electron-pair bond between two radical fragments A$^\bullet$ and B$^\bullet$ (where A and B are either identical or different). These are the covalent structure, Φ_{cov}, and the two ionic structures, $\Phi_{ion(1)}$ and $\Phi_{ion(2)}$.

For classical covalent-bonds, in Figure 1b, Φ_{cov} is significantly stabilized relative to the dissociation limit (A$^\bullet$ + $^\bullet$B) by the covalent spin-pairing energy D_{cov}. The VB-mixing diagram depicted on the right side of Figure 1b, shows that the consequence of the covalent-ionic mixing is a further stabilization of the Lewis-bond state (Ψ_{bond}) by the resonance-energy quantity, $RE_{cov-ion}$, due to the covalent-ionic mixing. This mixing is common to homonuclear (A = B) as well as heteronuclear (A ≠ B) bonds (e.g., H-H, H-Cl). We refer to this quantity as the *charge-shift resonance energy*, RE_{CS},[21] since it is associated with the fluctuation of the electron-pair relative to the covalent structure. As we shall see later, the RE_{CS} quantity is the dominant quantity in the charge-shift bonding (CSB) motif.
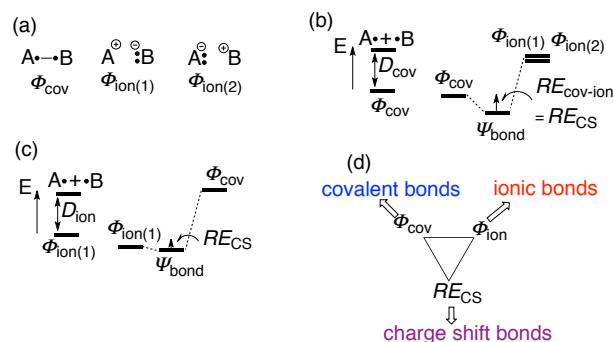

Figure 1. (a) Covalent (Φ_{cov}) and ionic ($\Phi_{ion(1)}$ and $\Phi_{ion(2)}$) VB-structures, which are required in order to describe electron-pair bonds between fragments A$^\bullet$ and B$^\bullet$. (b) and (c) describe the classical covalent and ionic bonds, respectively. The bond energy is dominated by either the spin pairing, D_{cov} (in b), or by the electrostatic stabilization between the ions (D_{ion} in c). The charge-shift resonance energy, RE_{CS}, further stabilizes the pure VB structures. (d) Emergent bond-families expected from the three variables/elements of bonding; covalent-, ionic- and charge-shift-bonds. Part (c) is adapted with permission of the RSC from Ref. 20.

Figure 1c shows the situation where one of the ionic structures, $\Phi_{ion(1)}$, is the lowest in energy. If this ionic structure is much lower than the covalent structure, as is the case for Na^+F^-, the resulting bond would be ionic, which may in principle enjoy some small RE_{CS} stabilization too (see Table S1 in the SI).

The above analysis shows that the electron-pair bond can be described in VB theory by three independent energy-components, which are indicated in the triangle in Figure 1d. Two corners of the triangle are occupied by the covalent and ionic VB-structures, while the third corner is the RE_{CS} quantity, due to the mixing of the two structures. In principle therefore, we might expect the following three distinct families of electron-pair-bonds that emerge from these distinct variables.[20]

One family is dominated by the covalent structure and its bond energy is primarily D_{cov}; prototype bonds are H-H, C-C, Si-Si, C-H, etc. The second family is dominated by the more stable ionic structure, $\Phi_{ion(1)}$, and its bonding-energy is dominated largely by the Coulomb attraction of the opposite charges D_{ion}; prototype bonds are Na^+F^-, Na^+Cl^-, etc. These are the two classical Pauling-Lewis families of covalent- and ionic-bonds. However, alongside the traditional families we may expect *in principle* to find a third family of bonds,[20] wherein most if not the entire bond-energy is provided by the RE_{CS} quantity. This is the charge-shift bonding (CSB) family.[21,28-31] Prototypical CSBs are F-F, O-O, H-F, C-F, Si-Cl, Au-Au, a variety of π-bonds in doubly and triply bonded elements, and so on.[31]

2.1. Why Did Pauling Miss the CSB?

The elements of Pauling's treatment, are outlined in Textbox 1, and the answer to the subtitle question is quite simple. Due to limitations of computing power in the 1930s, Pauling had to approximate the mixing between VB structures by semi-empirical means. He therefore assumed that in homonuclear bonds, like H-H, F-F, etc., RE_{CS} is <u>zero</u>.[14c] However, while for H-H this approximation is good, for F-F it is poor, since without RE_{CS} the F---F interaction is repulsive at all nuclear distances (see Figure 2b, later). But this is not limited to F-F. The assumption RE_{CS}(A-A) = 0 overlooks an entire bonding-family, where the RE_{CS} dominates the bonding. At the same time, this assumption ascribes RE_{CS} <u>only</u> to heteronuclear bonds, which differ in the electronegativities of the constituents.

As such, eventhough equation T3 (Textbox 1) predicts a continuum in the degree of iconicity (δ), in practice, the Pauling covalent-ionic superposition scheme became associated with two bond-families, based on a criterion of static charge-distribution; these are the covalent (polar-covalent) and ionic bond-families. In heteropolar bonds, the primary contribution to bonding was

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Textbox 1. In Pauling's original approach, the dissociation energy D_{AB} of an A-B bond was considered as being made of a purely covalent contribution, $D_{cov(A•-•B)}$, augmented by the resonance energy due to covalent-ionic mixing. The covalent contribution was estimated as the geometric-average of the bond-energies of the two corresponding homonuclear-bonds, A-A and B-B, as in equation T1a:

$$D_{cov(A•-•B)} = (D_{AA}•D_{BB})^{1/2} \tag{T1a}$$

$$RE_{Pauling}\text{(A-A or B-B)} = 0 \tag{T1b}$$

Using equations T1, the remaining contribution to the actual bond-energy, D_{AB}, was considered to be the resonance energy due to covalent-ionic mixing, and this value was used to gauge the electronegativity-scale (χ), as shown in equation T2 (in kcal mol⁻¹),

$$RE_{Pauling}\text{(A-B)} = D_{AB} - D_{cov(A•-•B)} = 23(\chi_A - \chi_B)^2 \tag{T2}$$

Furthermore, once the electronegativity is known, the "bond polarity" (δ) can be quantified as in equation T3, thereby providing the extent of ionic A^+B^- character in the bond:

$$\delta = 1 - \exp[-0.25(\chi_B - \chi_A)^2] \tag{T3}$$

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normally considered to be the D_{cov} quantity,[14c] while the covalent-ionic (charge-shift) resonance energy was of secondary/minor importance, except for very-polar bonds involving the most electronegative atoms (e.g., H-F). Furthermore, as shown by equations T2 and T3 in Textbox 1, the magnitude of $RE_{Pauling}$ was considered to vary in proportion to the electronegativity difference of the fragments, A and B, much like the charge distribution, i.e. the "bond-polarity" in equation T3. *Thus, semi-empirical VB calculations, completely overlooked the CSB family*

3. Bond Families Articulated by Ab Initio VB-Theory

The three bond families flesh out from *ab-initio* VB-calculations in Figure 2, which displays the dissociation-energy curves of six bonds that display the dominant VB structure of the bond alongside the "exact" VB-ground-state, which is a resonating combination of the covalent and ionic components, calculated by means of *ab-initio* VB theory.

Inspection of Figures 2a and 2b underscores the fact that the H-H and F-F bonds are entirely different. While in H_2 the covalent VB-structure displays by itself a potential well, which is already a good approximation to the exact curve (Figure 2a), the covalent component of F_2 is, on the contrary, purely *repulsive* (Figure 2b). Thus, covalent spin-pairing does not contribute any F-F bonding.
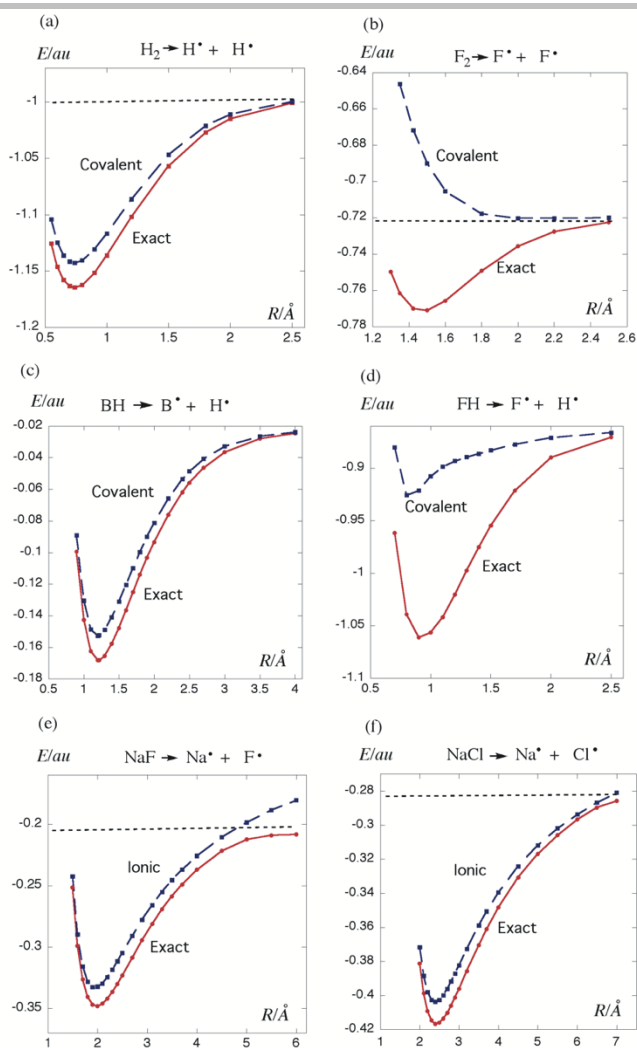
Figure 2. Six frames, (a)-(f), exemplifying the three bond-families (indicated in Fig. 1d). The frames trace the bond dissociation energy (in au) plots vs. the distances R(Å) between the atoms/fragments, for the bonds indicated by the dissociation processes on the top of the frames. In each case, the red curve is the exact VB curve, while the blue one is the energy of the dominant VB-structure. Covalent-bonds are shown in (a) and (c), ionic-bonds in (e) and (f), while charge-shift bonds (CSBs) in (b) and (d). Calculations are done at the highest VB level (the breathing-orbital VB (BOVB); see SI).Reproduced with permission from Ref. 21. Copyright 2009. Rights Managed by Nature Publishing Group.

The F-F bonding is in fact sustained by the very large charge-shift resonance-energy (62.2 kcal mol^{-1}) due to the mixing of the higher-lying ionic-structures (not shown in the Figure) into the repulsive covalent-structure.[21,28,30] Thus, although F-F may be formally considered as a covalent-bond, since it lacks static-ionicity, this definition cannot tag the true nature of the bond. The F-F bond is in fact a charge-shift bond (CSB), because *the bonding transpires as a result of the ionic-covalent fluctuation of the electron pair density.*

The case of F-F shows that the assumption underlying the classical Pauling scheme (Eq. T1b, Textbox 1) was inaccurate; the covalent structure by itself is not necessarily stabilizing even for homopolar bonds such as F-F where the covalent structure possesses the highest weight in the wave function. Importantly, many **homopolar bonds have large charge-shift resonance**

energies. Moreover, the appearance of a repulsive covalent-structure shows that when the covalent spin-pairing energy is frustrated by Pauli-repulsion from neighboring electron pairs (lone-pairs, bond-pairs, etc.), *there appears a new bonding motif where RE$_{CS}$ dominates the bonding*. Thus, once the assumption in Pauling's scheme [RE$_{CS}$(A-A) = 0] is removed, this enables re-charting of the mental-map of the chemical-bond.

Indeed, CSB is not restricted to F-F, as can be seen by comparing Figures 2d to 2c. It is clear that the B-H bond is classically covalent, while the F-H bond is not. The covalent structure for F-H is weakly bonded while the majority of bonding energy in the exact VB wave function arises from the RE$_{CS}$ due to the mixing of the ionic structures. Thus, here the Pauli repulsion weakens very much the covalent-bonding, but understandably not to the extent found in Figure 2b for F-F.

Finally, Figures 2e,f show NaF and NaCl. It is clear that for both bonds, the dominant VB-structure is ionic, and it is very close to the exact covalent-ionic superposition curve, with a negligible RE$_{CS}$ contribution (5-7.7%). These are classical ionic-bonds.

As such, Figure 2 reproduces the two classical bond-families, covalent and ionic, and it reveals also the presence of a third bond-type *wherein the bonding does not arise from any one of the structures, covalent or ionic, but rather from the resonance interaction, RE$_{CS}$, between them.* This is the charge-shift bonding (CSB) family. In recent years, a variety of σ- and π-bonds, both homo- and hetero-nuclear, were shown to share this property, thereby forming a growing family of CSBs.[21,28,30,31] Table S1 in the supporting information (SI) document collects more of these bonds.

4. Molecular Orbital (MO) and DFT-Based Theories Reveal CSB

At this point one may wonder if CSB is or is not a peculiarity of VB theory? The answer is "NO". In MO-calculations, the RE$_{CS}$ quantity of a bond *is embedded in the total energy* and is not an immediately apparent property.

The reference state for MO theory is the Hartree-Fock (HF) wave function, which lacks electron correlation corrections and for homonuclear bonds, its wave function contains 50% covalent and 50% ionic characters.[32] In fact, since in most electron-pair bonds, *the unbound fragments are radicals, the natural reference state for electron-pair bonding involves the spin-coupled open-shell radicals, i.e., the covalent-structure.* Therefore Ψ$_{HF}$ is not too useful as a reference for gauging bonding in F-F or for any bond for that matter. On the other hand, in the VB description of the bond, the covalent-structure, in which the two bonding electrons are fully correlated, serves as this requisite reference state.[21,22,32]

Fortunately, since MO and VB wavefunctions are mutually transformable, one can define the requisite open-shell reference from a two-configuration SCF (TCSCF) and derive thereby CSB and covalent bonds directly from an MO-based wavefunction. Let us follow with a brief summary based on the original study.[22,30]

Figure 3 shows the energy curves for the dissociation of H_2 (Figs. 3a,b) and F_2 (Figs. 3c,d) using MO-based and VB theories. In the VB-computed curves (Figs. 3b,d), the bond wavefunction is a superposition of the covalent- and ionic-structures, and the reference-state is the covalent-structure, as shown already above in Figures 2a,b. On the other hand, in the MO-based curves (Figs. 3a,c) the bond is described by a TCSCF wavefunction, using a reference two-configuration (RTC) state. The construction of the RTC state is based on the fact that a bond in the HF wave function, Ψ_{HF}, involves 50% covalent and 50% ionic characters, and so does the corresponding doubly-excited configuration, Ψ_D (where the two electrons in the σ-bond orbital are excited to the corresponding σ^*-orbital). In a homonuclear-bond, the only difference is the sign of the combination of the two structures, Ψ_{HF} = cov + ion, while Ψ_D = cov − ion.[33] Thus, subtracting Ψ_{HF} - Ψ_D, gives rise to the RTC state, which is the open-shell equivalent of the covalent VB-structure.
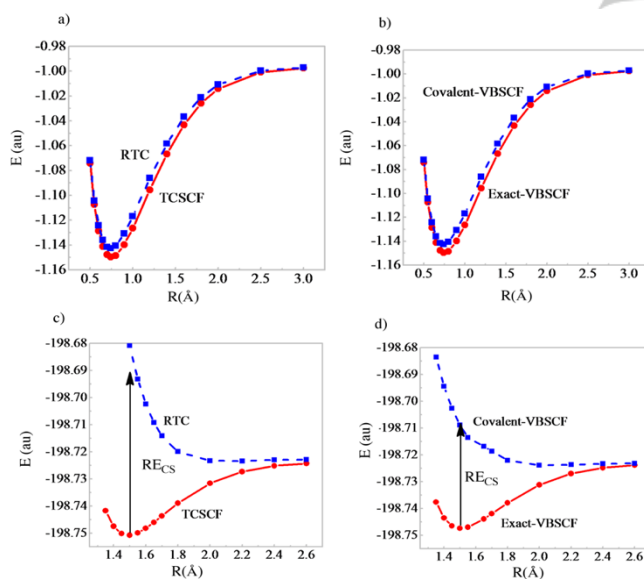

Figure 3. Full state- and reference-state curves for H-H and F-F bonds. The MO-generated curves involve two-configuration self-consistent field (TCSCF) wavefunctions and reference two-configuration (RTC) states, while the VBSCF curves are covalent and full covalent-ionic state curves (VBSCF is approximately equivalent to TCSCF): (a) and (b) show the dissociation curves for H-H. (c) and (d) show the corresponding curves for F-F. The vertical arrow for F-F shows the magnitude of the RE_{CS} as the difference between the reference-state (covalent or RTC) and the full state-curve. Reproduced with ACS permission from Ref 22.

It is seen from Figure 3, that the so-generated MO-based curves are entirely identical to the corresponding VBSCF curves; one for H_2 showing a classical covalent-bond, the other for F_2 showing CSB. The bond energies (D_e in kcal·mol⁻¹) are ~95 (H_2)

and ~20 (F_2) for both TCSCF and VBSCF. As we shift to the higher VB level in Figs. 2a,b these values change to 105.4 (H_2) and 36.6 (F_2) kcal·mol⁻¹, which are close within 1-3% to the corresponding experimental data (104.2 and 37.9 kcal·mol⁻¹). In both cases, the improvement of the bond-energy, but especially so in F_2 (by 83%), is due to increase of RE_{CS} as a result of covalent-ionic mixing.

Indeed, it is also possible to define the MO-based curves at higher levels, and compare them with the higher VB level (BOVB), and doing so for other bonds as well. This is illustrated in Figure 4, which shows the correlation of %RE_{CS} values obtained with TCSCF augmented with second-order perturbation-theory (PT2) and those obtained with the breathing-orbital-VB (BOVB) method, for the C-C, N-N, O-O and F-F bonds. The correlation is seen to be good and to involve classical covalent bonds (%RE_{CS} < 50) and CSBs (%RE_{CS} >> 50).

Clearly, CSB type of bonding is not peculiar to VB-theory. This bonding feature is **embedded** in MO-based wavefunctions, and is hence derivable from a TCSCF MO-based theory by a simple transformation. Moreover, the recently developed energy decomposition analysis (EDA) which is based on the pure-spin extension of the absolutely localized MO (ALMO) method,[23] was applied to DFT functionals, and demonstrated the presence of CSB for a variety of bonds, like F-F, and Mn-Mn (in $Mn_2(CO)_{10}$). As shown in Table S1 the CSB nature of the Mn-Mn bond in $Mn_2(CO)_{10}$ emerges also from VB calculations (RE_{CS} > 90%), and leading to a match between two-unrelated-approaches; EDA-DFT[23] and VB.
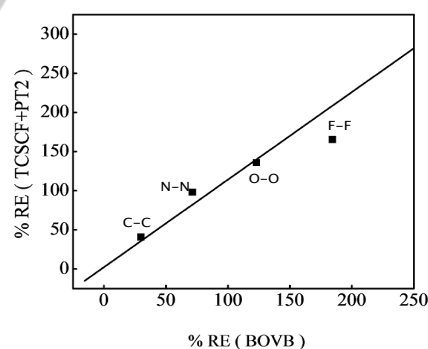

Figure 4. A correlation of %RE_{CS} values (%RE_{CS} = 100RE_{CS}/D_e) obtained at the TCSCF+PT2 level and the breathing-orbital VB (BOVB) level, for the C-C, O-O, N-N and F-F bonds, from left-to-right. Adapted with ACS permission from Ref. 22.

In principle, CSB could be derivable as well from DFT-based energy curves using densities (ρ) that correspond to two/multi-configuration DFT approaches.[34,35] *It follows therefore that the charge-shift resonance energy is a fundamental property of the chemical bond and is not specific to VB theory.* This conclusion will be reinforced below by electron-density analyses, which are independent of the computational method, VB, MO-CI or DFT.

5. Origins of Charge-Shift Bonding

5.1. Pauli Repulsion Pressure

As we saw, CSB is encountered whenever the electron-pair bond is surrounded by lone pairs, e.g., in F-F, Cl-Cl, O-O, S-S, H-F, C-F, etc. (see Table S1).[36] The failure of the respective covalent-structures of these bonds to provide significant bonding-energy, was found to be rooted primarily in *the Pauli-repulsion between the bonding electrons and adjacent electron-pairs that have the same symmetry as the bond*.[28,31,37,38] Two different cases of Pauli repulsion are exemplified in Figure 5.

Figure 5a illustrates this repulsive interaction that counteracts the spin-pairing stabilization in F-F. The repulsion is half as much in bonds like H-F, and the corresponding covalent structure exhibits bonding, but only marginally so.

Another example which is depicted in Figure 5b is [1.1.1]propellane that possesses an inverted-central C-C bond. It is seen that the inverted C-C bond is embedded inside a cage of six wing-C-C bonds, which apply on it Pauli-repulsion pressure. Making symmetry-adapted combinations of the six localized wing bond-orbitals (σ_w), one finds that two of the combinations possess the same symmetry as the inverted-C-C bond, and with respective electron-densities projected on the inverted-bond. One of these is a cage-orbital (σ_{cage}), which consists of three lobes pointing from the CH_2 moieties of the propellane to the center of the inverted-bond, and the second one is the all-positive combination of the wing orbitals that projects on the axis (σ_{axis}). These two electron pairs repel (by Pauli-repulsion) the covalent structure of the inverted bond, making it repulsive much like in F-F.[37] As we demonstrated,[38] it is possible to articulate the CSB concept, and manipulate the extent of Pauli repulsions, and hence also the CSB character, by changing the nature of the CH_2 bridges (e.g., to O, NH, BH, C=O, CF_2), and by expanding the three-wings of the central C-C bond to [3.3.3]propellane. The so-generated family of propellanes ehibits markedly different Pauli repulsion as well as the bonding-type, which spans the range from CSB to classical covalent.
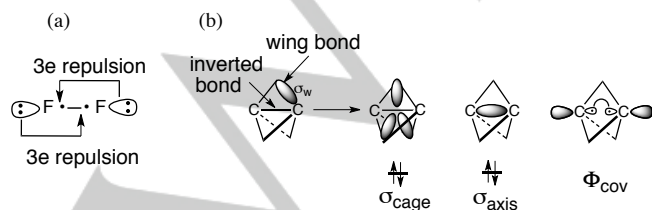

Figure 5. (a) The lone-pair bond-pair repulsion in the covalent-structure of F-F. The covalent-structure is depicted as two electrons (dots) connected by a line. (b) A cartoon showing the Pauli-pressure on the inverted-C-C bond of [1.1.1]propellane that is brought about by the six wing-C-C bonds. A localized wing-bond orbital is depicted and labelled as σ_w.

The expressions for the Pauli repulsion are discussed in Textbox S1. The *Pauli repulsion raises the kinetic energy* (T) of the electron-pair, thus disturbing the balance between the kinetic energy (T) and the potential energy (V) as required by the virial theorem for a bond in equilibrium, as shown in Eq. 1:[39]

$$T/-V = 0.5 \qquad\qquad (1)$$

Since RE_{CS} is dominated by the reduced-kinetic-energy and *is a negative quantity*,[39,40] the only way for the molecule to restore the virial-ratio, and achieve equilibrium bonding, is to augment the ionic component and increase thereby the CS-resonance energy,[21,31a,40] which lowers the kinetic-energy in the bonding region. This is the origin of the large RE_{CS} quantities of all CSBs, which we encountered.

It should be noted that this bonding-mechanism is quite different from the one used by classical covalent bonds to satisfy the virial ratio. In covalent bonds, e.g. H-H or C-C, which are devoid of adjacent lone pair repulsions, or have only weak Pauli repulsions, the primary effect that transpires when the two fragments are brought together and can overlap, *is a kinetic energy lowering (KEL)*, that tips the virial-ratio off-balance (eq. 1). At the purely covalent level, which is approximately so for H-H, the only degree-of-freedom for restoring the virial-ratio is by orbital shrinkage, which raises the atomic kinetic energy and lowers the corresponding potential energy (since the bonding electrons approach the nuclei), to the extent needed to re-establish the virial ratio.

By contrast, in CSBs there is already **excessive kinetic energy** that is caused by the Pauli-repulsion pressure, and as such, orbital shrinkage will aggravate the V-T imbalance. Hence, orbital-shrinkage ceases to be the dominant mechanism for restoring the virial-ratio. Indeed, as we noted for CSBs[40] e.g. in F-F, the orbital compactness of the two F˙ species remain practically unchanged when forming an F-F bond. Thus, orbital-shrinkage, which is the primary mechanism of bonding in classical covalent-bonds, is gradually replaced by the charge-shift resonance, as the bond approaches the CSB regime.

This is illustrated graphically in Figure 6, for a series of homopolar bonds having the same number of valence electrons around the bonded atoms, H_3C-CH_3, H_2N-NH_2, Cl-Cl, HO-OH, and F-F. The plot exhibits an inverse relationship between the bond-orbital contraction, gauged by compactness index $I_c(rel)$, and the degree of charge-shift character of the bond given by $\%RE_{CS}$. Hence, *as the $\%RE_{CS}$ of the bond increases*, *the orbital-shrinkage becomes less and less sgnificant*.
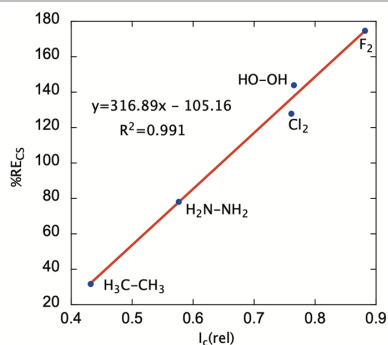
Figure 6. A plot of $\%RE_{CS}$ ($100 \cdot RE_{CS}/D_e$) vs. the compactness index I_c(rel) of the bond-orbitals, at the equilibrium bond distance, relative to the orbitals of the separated fragments (I_c itself is the ratio of the squared coefficients of the inner to the outer valence orbitals). A small value of I_c(rel) corresponds to a significant orbital-shrinkage, a value of I_c(rel) = 1.0 corresponds to no shrinkage.[40]

Thus, the relationship between the two quantities in Figure 6, shows clearly that the orbital-contraction mechanism becomes less important as the CS character of the bond increases along the series C-C, N-N, Cl-Cl, O-O, and F-F.[40] As such, while the restoration of the virial-ratio of covalent bonds (C-C) is governed by **orbital shrinkage, which is needed for raising the kinetic energy,** for the CSBs (e.g., Cl-Cl, O-O, F-F) **the rise in the kinetic energy, inherent tot he Pauli repulsion, is mitigated by RE_{CS},** while orbital-contraction becomes secondary.

In summary, CSB will be encountered in bonds of atoms (fragments), which are electronegative and/or lone-pair rich, and in bonds encased in environments which exert large Pauli-repulsion pressure, like the central-bonds in propellanes. In transition-metal dimers, wherein the metal is rich in d-electron occupancy in the valence-shell (e.g., Au, Cu, Ag), the doubly occupied d-orbitals will play the role of lone-pairs, and will generate CSBs.[29] Similarly, in transition metal-complexes which contain metal-metal bonds encased within many electron-pair bonds, the metal-metal bond will correspond to CSB, as demonstrated[23b] for the Mn-Mn bond in $(CO)_5Mn-Mn(CO)_5$, and reproduced by us in this study (Table S1).

The Pauli-repulsion pressure is the root cause for the charge-shift character of these bonds, with the consequence that their bonding mechanism differs from that of covalent-bonds: while significant orbital shrinkage is a necessary condition for covalent-bond formation, it is not so for CSBs which replace this mechanism by the strongly stabilizing covalent-ionic resonance.

5.2. Additional CSB Factors

An additional CSB factor[28,31a,c,d] was found in bonds between metalloids of Group-14 and electronegative elements, like the Si-Cl and Ge-Cl bonds (Table S1). The VB calculations for these bonds[28,31c,d;41] show that the corresponding ionic-curve for e.g., the Me_3Si-Cl (Si-Cl in general) bond is much deeper than

the corresponding one for Me_3C-Cl (C-Cl in general) bond. Moreover, the ionic-curve $Me_3Si^+Cl^-$ is located at a shorter distance compared with the one for $Me_3C^+Cl^-$. The tighter Si---Cl distance of the ion-pair curve owes it origins to the charge distribution in the cation, as shown in Figure 7 for Me_3Si^+ vs. Me_3C^+. Thus, in Me_3Si^+ the charge is completely localized on Si (+2.0) and the CH_3 substituents carry a negative-charge, whereas Me_3C^+ is highly delocalized, such that the central carbon has a small charge (+0.6). This difference would enable the anion to approach Si (in Me_3Si^+) along the Si---Cl axis closer than it can approach carbon in Me_3C^+. As such, the electrostatic stabilization of the ionic-structure Si^+Cl^- is always significantly larger than in C^+Cl^-, and the corresponding minimum is also tighter. This causes a stronger ionic-covalent mixing in Me_3SiCl, thus leading also to high RE_{CS} values. As such, *Si-Cl bonds are both more ionic and have higher CSB characters compared with C-Cl bonds* (see e.g., the H_3Si-Cl bond in Table S1 has RE_{CS} = 65 kcal mol^{-1} vs. 46 kcal mol^{-1} for H_3C-Cl).
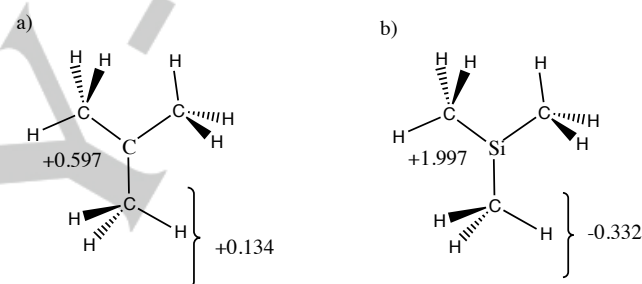

Figure 7. NBO charge distribution on Me_3C^+ and Me_3Si^+ (calculated by NBO using B3LYP/cc-pVTZ level).

As we shall see later the short distance in the ionic structure enhances the CSB character in bonds to silyl-groups and affect the chemical behaviors in condensed phases.

6. Charge-Shift Bonding in Dative and Coordinative Bonds

Dative- and coordinative-bonds are widespread in main-elements[18,19] and transition-metal complexes. These bonds are formed between one fragment which possesses a vacant orbital in the valence-shell, and another one that possesses an easily-donated electron-pair, such as a lone-pair or a π-pair. As such, many of these bonds are supported by charge-shift resonance energies and are therefore CSBs. Below we discuss a few examples of such bonds.

Figure 8 shows two examples. One, in Figure 8a, involves borane (BH_3) and ammonia (NH_3). It is seen that at the equilibrium N-B bond distance, the lowest VB-structure is the "no-bond" one, in which the two molecules interact by weak intermolecular-interactions. Above it there lies an open-shell singlet-pair structure, in which the ammonia transferred a single

electron to the borane, and the two odd electrons underwent spin-pairing. By analogy to the terminology for electron-pair bonding, the electron-transferred structure is the HL structure, and is hence labeled as Φ_{cov}, while the "no-bond" structure is analogous to one of the "ionic" structures of the electron pair, hence Φ_{ion} (the second ionic structure, H_3N^{2+} $:BH_3^{2-}$ is insignificant. See Table S2).

In Figure 8a, it is clear that the only N-B bonding mechanism that can emerge from these two VB structures is a CSB due to the mixing of Φ_{cov} into Φ_{ion}. The corresponding RE_{CS} shown underneath the VB mixing diagram is 42.1 kcal mol^{-1}, and is higher than the corresponding bond-energy ($\%RE_{CS}$ = 110). As such, the bond is a CSB.[42] A similar situation was found for the related molecule, H_3N-BF_3 (Table S2).

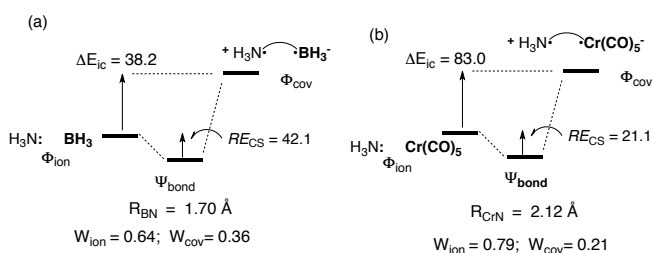**Figure 8.** VB-mixing diagrams for, (a) the dative-bond (Ψ_{bond}) in H_3N-BH_3, due to mixing of Φ_{ion} (N: B) and Φ_{cov} (⁺N• •B⁻); and (b) the coordinative-bond in H_3N-$Cr(CO)_5$, due to mixing of Φ_{ion} (N: Cr) and Φ_{cov} (⁺N• •Cr⁻). Beneath each diagram we indicate the bond length (R in Å), the charge-shift resonance energy (RE_{CS}, kcal·mol^{-1}), the energy gap between the VB-structures (ΔE_{ic}, kcal·mol^{-1}), and the weights (W) of the corresponding structures.

Figure 8b depicts the VB-mixing diagram for a bond between ammonia (NH_3) and chromium pentacarbonyl ($Cr(CO)_5$). The latter fragment is isolobal to BH_3.[43] Once again, at the equilibrium N-Cr bond distance, the lowest VB structure is the "no-bond" one, i.e. the formally "ionic" structure, N: Cr, which has some weak nonbonded-interactions. 83 kcal mol^{-1} above it there lies the covalent structure, (⁺N• •Cr⁻) in which the two single electrons are spin-paired. As in the above dative-bond, here too, the only N-Cr bonding that may emerge is due to the mixing of these two VB structures, and is hence a CSB. The corresponding RE_{CS} shown underneath the VB mixing diagram is 67% of the corresponding bond energy (Table S2: BDE = 31.4 kcal·mol^{-1} relative to separated H_3N: + $Cr(CO)_5$).

Examples of L-$Cr(CO)_5$ with L-Cr bond being CSBs are abundant and easily predictable. Furthermore, there exist numerous coordinative-bonds between amines, amino acids, and DNA fragments with main-element- and transition-metal cations, like Cu^+, Zn^{2+}, Al^{3+}, and so on, which are all CSBs. These bonds play a key role in brain chemistry.[44]

7. Charge-shift Bonding in Hypervalent (3-Center-4-Electron) Systems

Second- and third-row elements as well heavy noble gases, can form molecules with coordination-numbers that exceed the number of electron pairs „allowed" by the Lewis–Langmuir valence rules allowed. XeF_2, $XeCl_2$, KrF_2, RnF_2, ClF_3, SF_4, and PCl_5 are a few of these intriguing molecules. As articulated in the Rundle-Pimentel model,[45] these molecules, which are referred to as "hypervalent", involve 3-center-4-electron (3c/4e) bonds, which increase the coordination-number of the central atom, in formal violation of the Octet-Rule. Xenon-difluoride, XeF_2, is a prototypical hypervalent molecule, having a linear F-Xe-F structure, which involves a 3c/4e-bond of 64.1 kcal·mol^{-1} relative to the dissociation limit,[46] despite the fact that Xe is a noble gas.

In a nutshell, the Rundle/Pimentel-model restricts the reasoning to the three axially-oriented orbitals that are involved in the linear 3c/4e σ-bonding, exemplified in Figure 9. These fragment-orbitals give rise to three MOs; respectively bonding, non-bonding and antibonding. Since the two occupied MOs are either strongly bonding or nonbonding, some stability is expected for the 3c/4e σ-bond.
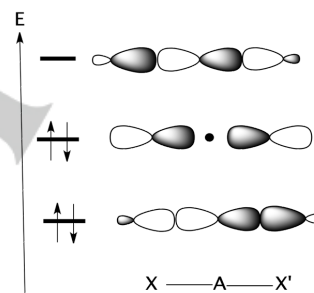

Figure 9. The Molecular orbitals of a 3c/4e σ-bond in an hypervalent X-A-X' molecule, where A and X are main elements having an axial np orbital. Topologically-equivalent MO diagrams can be generated when the three fragment orbitals are ns types, or when the central A uses only an ns orbital.

Since all 3c/4e species, even 3c/4e transition states, share the same MO topology as in Figure 9, the above simple rationale of MO occupancy suggests that in principle, all 3c/4e hypervalent-species should be stable. This is obviously not the case. As an example, among many, this simple model fails to account for the fact that the 3c/4e H_3^- species is a transition state and is unstable, whereas the isoelectronic F_3^- anion is stable. Clearly then, the Rundle/Pimente- model misses key factors that impart stability to the 3c/4e species. These factors appear lucidly in the VB projection of the MO- model, as originally proposed by Coulson.[47] Indeed, using VB theory, some of the present authors[48,49,50] have recently shown that the stable 3c/4e bonds[51] are CSBs. This is demonstrated below.

In the VB-projected Rundle-Pimentel MO-configuration[47] the electronic structure of an X-A-X' linear molecule is described as a combination of the four VB structures, in eq. 2:

X-A-X' = X•–•A$^+$:X'$^-$ ↔ X:$^-$ A$^+$•–•X' ↔ X:$^-$ A^{2+} :X'$^-$ ↔ •X A: X'• (2)
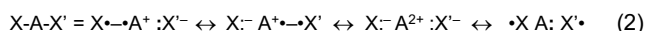
The first two VB structures display a covalent bond between the A and X or X' fragments, while the third structure is quadruply-ionic, and the last one is a singlet diradical, in which the terminally located single-electrons are paired to a singlet-spin state.

Considering an archetypical hypervalent molecule, XeF_2, one finds that none of the four VB-structures of Eq. 2 is by itself bonded relative to the dissociation limit, Xe + 2F•.[48] It follows that this molecule owes its entire stability to a very large resonance-energy arising from the mixing of the four VB-structures. This condition can be met, however, only if the normal-valent compound, here F-Xe$^+$, is a CSB. Indeed, our VB analysis of the stable hypervalency in PF_5, ClF_3 and SF_n (n= 1, 2, 4, 6) verifies that in all cases, the normal-valent bond is a CSB.[49] Thus, the general model for hypervalence in 3c/4e electron-rich systems appears to be the VB-version of the Rundle-Pimentel model, *coupled with the presence of charge-shift bonding due to mixing of covalent and ionic structures*.

Figure 10 shows the VB-mixing diagram for the four VB-structures, taken from our recent study of F-Xe-F'.[48] It is seen that all the VB-structures are higher than the dissociation limit (Xe + 2F•, with E defined as zero) and hence do not intrinsically contribute to F-Xe-F' bonding. The lowest VB-structure is the quadrupl- ionic one, F:$^-$ Xe^{2+} :F'$^-$, which is 79 kcal/mol higher than the dissociation limit, while the other three VB-structures are higher in energy by 26 kcal/mol or more. With these small energy gaps among the VB structures, and the fact that F-Xe$^+$ is itself a CSB, the mixing of the four VB-structures is intense, resulting in RE_{CS} = 127.5 kcal/mol (%RE_{CS} > 200), which is twice as large as the value for the F-Xe$^+$ electron-pair bond.

Based on the VB-mixing diagram, the pre-requisites for hypervalency in molecules of the X-A-X' type, are: (i) low *first and second* ionization potentials, for A, and (ii) ligands being prone to CSB in normal-valent species (i.e. being electronegative and bearing lone pairs). Lack of any of these features explains the many exceptions to the traditional Rundle/Pimentel-model, like the instability of F-Ar-F, OF_n, and so on.
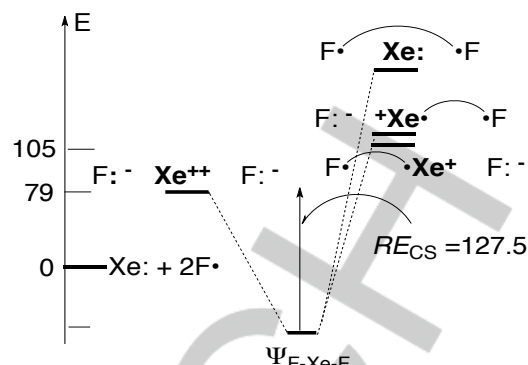

Figure 10. VB-mixing diagrams for the 3c/4e-bond in F-Xe-F. The energies of the structures (E in kcal·mol^{-1}) are relative to the dissociation limit (Xe + 2F•) defined as the zero energy (E=0). Data are taken from Ref. 48.

8. Comparison of CSB vs. Covalent-Bonding Using Electron Density Analyses

The molecular electron-density, ρ, is an observable quantity that provides information about the nature of the bond. As such, we shall discuss briefly the main analytical tools of the electron density; via Electron Localization Functions (ELF), the Laplacian in QTAIM, and the mechanical properties of the electron density tensor of the bond.

8.1. CSB Emerges from ELF Analysis:

ELF provides the means to generate a space partition of the electron densities into core-electrons, lone-pairs and bond regions. The bonding-region is defined as a disynaptic-basin between two atoms/fragments (A and B), and its total electron-density population, $\bar{N}_{AB}$, can be integrated and used to characterize the A-B bond within the molecule.[27] Generally speaking, kosher covalent-bonds are typified by $\bar{N}_{AB}$ ~ 2, while ionic bonds like Na$^+$Cl$^-$ feature only mono-synaptic basins. Table S3 provides data for 19 electron-pair bonds,[28] which clearly reveal the three bond-families. Thus, while covalent bonds like H-H have $\bar{N}_{AB}$ ~ 2, CSBs like F-F, C-Cl, etc. possess $\bar{N}_{AB}$ <1, and Na$^+$Cl$^-$ and Na$^+$F$^-$ have only monosynaptic basins.

Moreover, the ELF analysis provides a quantity that is directly related to the physics of the bond: the variance $\sigma^2[\bar{N}_{AB}]$, which measures the degree of fluctuation of the electron-density in the respective bonding-basins. In accord, it can be seen (Table S3) that in all CSBs, the variance is close to the basin-population, while in classical-covalent bonds the variance is significantly smaller than the population (about twice smaller).

8.2. CSB Emerges from AIM Laplacian-Analysis

In QTAIM theory,[24] an interaction between atoms/fragments is generally characterized by a bond-path, which defines a maximum-density path connecting the interacting atoms. The point of the path at which the density is at minimum is called the bond critical point (BCP), and the corresponding values of the density, $\rho(r_c)$, and its Laplacian $\nabla^2\rho(r_c)$ at this point are characteristics of the interaction type in the bonding region.[24] The Laplacian (Lap) of a bond sums the kinetic ($G(r_c)$) and potential ($V(r_c)$) energy-densities at the BCP, by the local-virial theorem expression in Eq. 3:

$$\frac{\hbar^2}{4m}\nabla^2\rho(r_c) = 2G(r_c) + V(r_c) \qquad (3)$$

A negative Laplacian means that the bonding-region is dominated by electron-sharing and lowering of the potential energy, while a positive Laplacian means that the shared-density in the bonding-region is typified by excess kinetic energy-density, $G(r_c)$, and is hence repulsive. All the QTAIM parameters for bonds in a molecule can be either calculated or derived from experimental density determination, and are used by experimental chemists to characterize interactions within molecules.[52-55] As such, QTAIM is very useful and one might expect it to tag the presence of CSBs, in those cases which are typified by excess Pauli repulsion in the bonding region (see Table S1, S2).

8.3. ELF and QTAIM Analyses of Covalent-Bonds vs CSBs

Figure 11 highlights the distinction of the covalent and CSB families by the three theoretical approaches. The figure depicts the ELF bonding-basins for H_3C-CH_3, F-F and the wing- and inverted- C-C bonds types in [1.1.1]propellane, alongside their VB and QTAIM properties.

It is seen that the C-C bond of ethane (Figure 11a) and the wing-C-C bonds in [1.1.1]propellane (Figure 11c) all have: ELF disynaptic-basins with populations close to 2.0 with a variance σ^2 being two-fold smaller, highly negative Laplacians with significant densities at the bond-critical points, and a small or moderate RE_{CS}. These are classical-covalent bonds.

By contrast Figures 11b,c show that the disynaptic ELF-basins of F-F and the inverted-C-C bond of [1.1.1]propellane[56] are CSBs. The populations in their respective bond-regions are, split into two monosynaptic-basins, indicative of the Pauli-repulsion pressure. Furthermore, the Laplacians are highly positive, indicating the impact of Pauli repulsion, on the respective covalent-structures. And as expected for CSBs, the RE_{CS} quantities for the two bonds are very large, with significant fluctuations, of the bond shared-densities, indicated by the variance quantities that are as large as the populations.
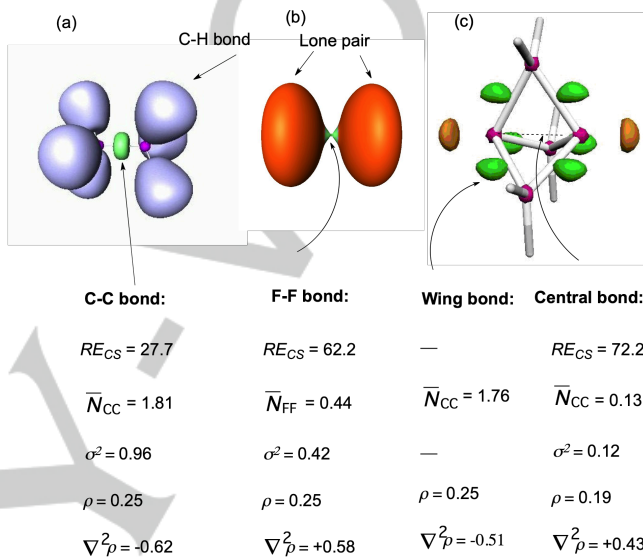

C-C bond:	F-F bond:	Wing bond:	Central bond:
$RE_{CS} = 27.7$	$RE_{CS} = 62.2$	—	$RE_{CS} = 72.2$
$\overline{N}_{CC} = 1.81$	$\overline{N}_{FF} = 0.44$	$\overline{N}_{CC} = 1.76$	$\overline{N}_{CC} = 0.13$
$\sigma^2 = 0.96$	$\sigma^2 = 0.42$	—	$\sigma^2 = 0.12$
$\rho = 0.25$	$\rho = 0.25$	$\rho = 0.25$	$\rho = 0.19$
$\nabla^2\rho = -0.62$	$\nabla^2\rho = +0.58$	$\nabla^2\rho = -0.51$	$\nabla^2\rho = +0.43$

Figure 11. Pictorial ELF representations of electron density in a few bonds: (a) the ELF disynaptic-basin[28] for H_3C-CH_3; (b) the disynaptic- and lone-pair-basins for the F-F bond; (c) green disynaptic-basins for the wing-bonds of [1.1.1]propellane, and two monosynaptic-basins for the central-inverted-bond. The inverted-bond is marked by dashes between the bridging carbon atoms.[56] Each bond is further characterized by its covalent-ionic resonance energy RE_{CS}, the ELF basin-population $\overline{N}$ and its variance σ^2, the density ρ at the bond-critical-point and the corresponding Laplacian $\nabla^2\rho$ (energies are in kcal·mol^{-1}, densities in ea_0^{-3}, Laplacians in ea_0^{-5}). For H_3C-CH_3 and F-F, the ELF and QTAIM data are theoretically computed.[28,37] respectively. For [1.1.1]propellane, the QTAIM parameters are experimental values[52] from the study of a substituted [1.1.1]propellane derivative. The ELF drawings in Figs. 11a-11c are reproduced from Ref. 30.

Thus, the three methods diagnose the same classification of the homonuclear-bonds into two families. ELF and QTAIM diagnose the attractive/repulsive nature of the covalent "shared-densities", while VB brings about energetic components that highlight the dominant role of the RE_{CS} energy in the CSB group. Note that the quoted QTAIM properties for [1.1.1]propellane are derived from experimental densities,[52] and as such, *lending experimental support to the characterization of the inverted C-C bond as CSB.* A similar consensus was recently reported for the O-O bond of Rubrene *endo*-peroxide,[54] for Mn-Mn and Mn-CO bonds in Mn_{10} $(CO)_{10}$,[55] as well as other bonds.[57-63]

8.4. Laplacian Profiles for CSB and Covalent Bonds

H-H and F-F are respectively, the two archetypes of the covalent and CSB bond-families. The difference between these two bonds is vividly seen in the profiles of the respective Laplacians, drawn in Figure 12 up to the interatomic distance of 4.5 Å. Hence, irrespective of the computational scheme used to generate these Laplacian-profiles, the respective shapes for the two bonds differ markedly.
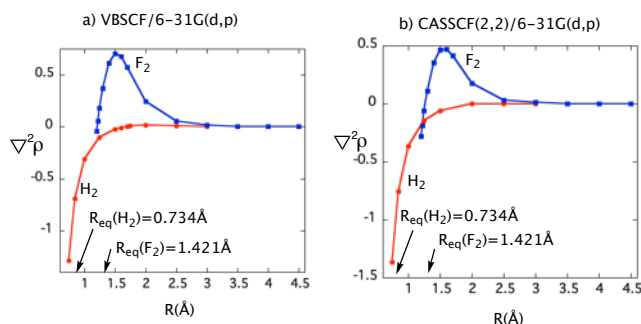

Figure 12. Laplacian profiles for H-H and F-F calculated by VBSCF (a) and CASSCF(2,2) (b). See also Figure S1.

There is nothing in these profiles that suggests that CSBs are simply stretched bonds, as argued recently.[64] Thus, at long distances, the Laplacian for H-H is virtually zero, and in the range near the equilibrium-distance, R = 2 - 0.75 Å, it descends rather fast and becomes strongly negative, as expected for a covalent-bond. In contrast, the respective Laplacian curve for F-F continuously rises from zero at the interval 4.5 - 3.0 Å, reaching a maximum positive-value near the equilibrium-distance of the bond, as expected for a CSB dominated by Pauli repulsion (Figure S1, shows the electron-densities in the bond critical-point).

At shorter F-F distances (1.2-1.1 Å) the Laplacian starts descending and becomes eventually negative at $R_{F-F} \leq 1.20$ Å.[65] To understand the mechanism of sign-changing of the Laplacian, we partitioned it to its covalent, ionic, and resonance density components.[66] In so-doing, we found that the covalent component of the Laplacian remains positive and approximately constant in the range of R_{FF} = 1.43 – 1.1 Å, while the ionic component becomes increasingly positive as the distance shortens. In contrast, the density-component due to covalent-ionic-resonance becomes increasingly more negative (-2.777) and it overrides the positive Laplacians of the covalent and ionic densities (Table S4).

As we showed originally,[66] the Laplacian of the resonance-density correlates with RE_{CS}; *the larger the RE_{CS} quantity, the more negative is the Laplacian of the resonance-density*. The VB calculations for F-F verify this expectation. Thus, at the short distances the weight of the ionic-structures increases and simultaneously, RE_{CS} increases to 96 kcal·mol^{-1} (from ~60 kcal·mol^{-1} at the equilibrium F-F distance R_{FF} = 1.43 Å), and this

increase is reflected in the highly negative covalent-ionic-resonance density-component of the Laplacian (Table S4). As such, *the mechanism that changes the sign of the Laplacian for F-F is entirely dominated by the charge-shift bonding*, and has nothing to do with the covalent interaction. By contrast, *in the covalent H-H bond, the Laplacian is entirely dominated by the covalent structure* throughout the interatomic distances used in Figure 12.

8.5. Laplacians of Dative, Coordinative and Hypervalent Bonds

In dative/coordinative/hypervalent bonds, where the leading VB-structure is the no-bond one, e.g. H_3N**:** BH_3 (called also ionic in Figure 8 above), or the ionic one e.g., F:$^-$ Xe^{2+} :F'$^-$, the Laplacian-value will reflect the balance of the positive no-bond component, and the negative resonance-density component, which correlates with RE_{CS}.[66,67] As shown in Scheme 1, all the N-B bonds possess a net positive Laplacian, e.g. 0.4-0.43 for H_3N-BH_3. Similarly, in H_3N-Cr(CO)$_5$ and other coordinative-bonds like, H_3N-Cu$^+$ and H_3N-Zn^{++} the Laplacians are positive (0.28-0.36 and 0.32-0.38, respectively). These results are similar to experimentally observed values for other coordinative-bonds.[55] Finally, the Laplacian of XeF$_2$ is positive, 0.232-0.234 for each of the Xe---F linkages.

H_3N-BH_3	H_3N-BF_3	F-Xe-F	H_3N-Cr(CO)$_5$	H_3N-Cu$^+$	H_3N-Zn^{++}
0.4029	*0.1734*	*0.2337*	*0.3568*	*0.3560*	*0.3369*
0.4250	**0.2164**	**0.2318**	**0.2835**	**0.3411**	**0.3213**
				0.3642	0.3801

Scheme 1. Laplacian values for the N-B bonds in H_3N-BH_3, H_3N-BF_3, and the N-metal bonds in H_3N-Cr(CO)$_5$, H_3N-Cu$^+$ and H_3N-Zn^{++}, as well as in F-Xe-F. The first line in the italic-font corresponds to the m06-2x/cc-pVTZ, the second line in bold-font corresponds to the mp2/cc-pVTZ and third line for H_3NCu^+ and H_3NZn^{2+} corresponds to the m06-2x/cc-pVTZ in water solution.

8.6. Electronic-Stress Tensor (EST) Analysis of the Density in Covalent Bonds vs. CSBs

The nature of bonds can be classified as-well from mechanical properties of the density, that are derived from the electronic-stress tensor.[25,26,68,69] The mechanical information is associated with three eigenvalues (λ_1- λ_3) of this density-tensor at the bond critical point (r_c). The tensile-mode, tangent to the bond axis, possesses an eigenvalue (λ_3), which indicates the extent whereby the electron density is attracted to the nuclei, while the compressive-modes, perpendicular to the bond axis, possess eigenvalues (λ_1 and λ_2) that indicate how much the electrons are attracted to the center of the bonding region.

As shown by Jenkins et al,[25,26] the tensor of covalent-bonds, is dominated by the compressive-modes ($\lambda_1 + \lambda_2$), while the one for CSBs is dominated by the tensile-eigenvalue (λ_3). These authors further showed that the ratio of the strength of the tensile-mode to the average of the compressive-modes, $\Lambda_{rel} = |\lambda_3/0.5(\lambda_1 + \lambda_2)|$, is a measure of the CSB character of a bond. These values are depicted for a few bonds in Figure 13, and are seen to increase as one moves from the covalent-bond (C-C) to the CSBs (O-O and F-F). The increase of the Λ_{rel} quantity is proportional to the corresponding %RE_{CS} of these bonds (see Fig. 4).
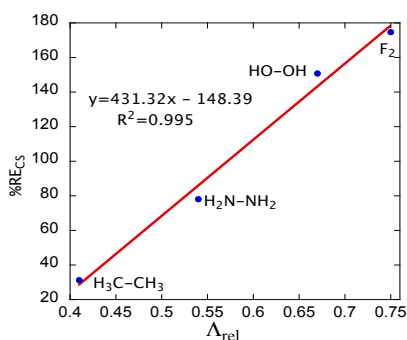

Figure 13. A plot of %RE_{CS} ($100(RE_{CS}/D_e)$) of some bonds vs. the mechanical properties, $\Lambda_{rel} = |\lambda_3/0.5(\lambda_1 + \lambda_2)|$, of these bonds at the bond critical points. The mechanical properties are derived from the electron-stress tensor of the density in Ref. 25. Not that the symbol we use (Λ_{rel}) is different than in Ref. 25 and 26 (Ξ).

This approach was further used by the authors[25] to derive bond-indicators based on the eigenvalues of the second-derivative tensor of the electron-density (more akin to the Laplacian). The latter values vary in the same manner as above, and are small (<1) for covalent bonds and large for CSBs; 0.69 (for C-C) vs. 2.0 (for O-O) and 2.7 (for F-F), again in the order of the respective RE_{CS} for these bonds.[25]

More recently, Jenkins et al[26] calculated the Λ_{rel} property for the inverted bond of [1.1.1]propellane at different levels. As shown in Scheme 2, the values for the inverted-bond, 3.4-3.8, are much smaller than those for the covalent wing-bonds (<1). The authors concluded that the inverted C-C bond is a CSB, with significant "metallicity" and polarizability.[26] This conclusion matches the respective computed Laplacians (Lap = +0.1 → +0.14 vs. -0.40→ -0.47, respectively[26]) and those quantified from experimental density,[52] for the inverted- vs. wing- C-C bonds.

$\Lambda_{rel} = 3.4 - 3.8$
Lap$= 0.10 \mapsto 0.14$

$\Lambda_{rel} = 0.81 - 0.89$
Lap$= -0.40 \mapsto -0.47$
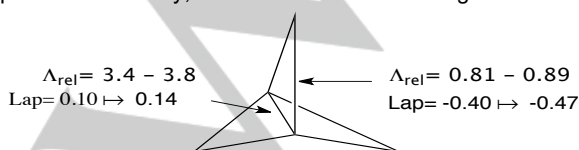
Scheme 2. The range of calculated (MP2 to CCSD(T) values) mechanical properties, $\Lambda_{rel} = |\lambda_3/0.5(\lambda_1 + \lambda_2)|$, and Laplacians (Lap) for the inverted- and wing-C-C bonds of [1.1.1]propellane, according to Ref. 26.

9. Experimental Manifestations of CSB

Let us discuss some experimental trends which project the properties of CSBs vs. other bond types (covalent and ionic).

9.1. Quantifying RE_{CS} from Experimental Data

A preliminary but essential question is whether the charge-shift resonance energy (RE_{CS}) can be quantified by experimental means? The answer is positive. Thus, the experimental activation energies[70] and the theoretically-calculated barriers[71] for the fluorine-atom exchange, H• + F-H' → H-F + •H' were found to be astonishingly large (more than 42 kcal mol⁻¹), compared to the barriers for the H transfer reaction, F• + H-F' → F-H + •F' (ca. 21 kcal mol⁻¹).[72] This large difference between the two barriers, and especially the magnitude of the barrier for the fluorine-exchange, were deemed quite surprising by the chemical community, for the reasons that: (i) energy barriers of radical reactions are generally rather low, and (ii) these barriers are governed by the strength of the bond being broken, which is actually the same F-H bond in both reactions. In fact, the trend is similar for all the halogens (X) in X• + H-X' → X-H + •X' vs. H• + X-H' → H-X + •H', though the barrier-differences are smaller, as might be expected from the fact that H-F is a CSB with a large RE$_{CS}$ while the remaining H-X (X = Cl, Br, I) molecules are normal polar-covalent bonds.[21,30]

As we have shown,[72] this activation-energy difference is rooted in the ionic-structures of the respective transition states (TSs), (X•••H•••X) vs. (H•••X•••H), of the two reactions that H-X molecules can undergo with X• or H• radicals. Thus as shown in Figure 14, the ionic-structures of the halogen-exchange reactions in (a) suffer from 3e-Pauli repulsion between the closed-shell X:⁻ anion and the H• radical. In contrast, the ionic-structures of the hydrogen-exchange TS in (b) are devoid of this Pauli repulsion. Consequently, the ionic-structures of the halide-exchange reaction are high in energy and will mix to a lesser extent with the covalent HL-state, and the respective TS will lose some charge-shift resonance energy, compared with the TS for the hydrogen-exchange reaction.
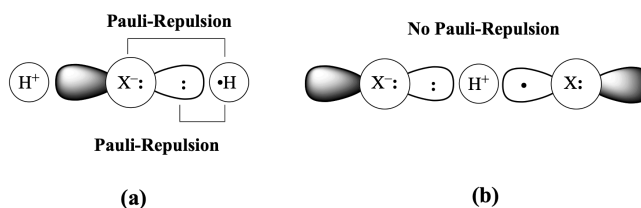

(a)   **(b)**

Figure 14. (a) 3e-Pauli-repulsions in an ionic-structure of the halogen-exchange TS (the mirror-image ionic-structure is not shown). (b) Absence of 3e-Pauli repulsions in an ionic-structure of the hydrogen-exchange TS.

Indeed, the barrier difference between the two series was found[72] to follow a very simple relationship: as ¼ of the RE_{CS} quantity of the H-X bond that undergoes cleavage during the two processes. Thus, RE_{CS} is given as:

$$RE_{CS(H-X)} \approx 4[\Delta E^{\ddagger}_{H/XH} - \Delta E^{\ddagger}_{X/HX}] \qquad (4)$$

As such, according to equation 4, measuring these barrier-differences enables one to quantify the respective CS resonance energies from experimental barriers. Other such series may be devised, which enable the quantification of RE_{CS} for other bonds. Let us mention the recent demonstration by Borden, Hoffmann et al[73] that the H-abstraction barrier by O_2 is high due to the resonance of the three-electron bonds of dioxygen, that were recently shown to be CSBs.[74] Therefore, the RE_{CS} quantity of bonds, has a status as the resonance-energy of benzene or other aromatics, and merits equal attention.

9.2. Comparison of Laplacian Values to Experimental Data

Since the molecular electron-density of molecules is an experimental property, it enables the derivation of bond properties, such as the Laplacian, ELF, and electronic-stress tensor (EST).[25-27,68,69] The example depicted in Figure 11c shows the experimentally derived Laplacians for the two bond types in [1.1.1]propellane.[52] The Laplacians are differently-signed, and demonstrate that the wing-C-C bonds are covalent-bonds, while the inverted central-C-C bond is a CSB. These assignments are in full accord with the conclusions of *ab initio* VB calculations[37] as well as MP2 and CCSD calculated values in Scheme 2.[26] The recent study of the O-O bond in the crystal-structure of Rubrene endo-peroxide shows an agreement between experiment and theory that the bond is a CSB. A similar finding pertains to the Mn-Mn bond in $Mn_2(CO)_{10}$, which is CSB[23] and its experimental and theoretical Laplacian values are positive.[55] Thus, electron density obtained from either experiment or theoretical calculations, leads to a positive Laplacian, and to other criteria that suit CSBs.[54] We are confident that other experimental electron-densities,[53] will enable the analysis of a variety of bonds by means of QTAIM, ELF and EST and will provides the means to explore the CSB territory.

9.3. Comparison of Experimental and Theoretical Predictions on the Nature of Si-X Bonds

R_3Si-X (X–electronegative atom/fragments, R–alkyl) bonds are highly ionic.[28,75] At the same time, since Si is less electronegative than the alkyl substituents, the Si atom accumulates a very high positive charge (+2, in Fig. 7). As already reported in section 5.2., this high Si charge enables the X− anion

to approach closely to Si+ along the Si----X axis, leading thereby to strong electrostatic interactions and sizeable ionic-covalent mixing (see Table S1). Indeed, by charge distribution, Si-X bonds seem to be virtually as ionic as e.g., NaCl.[28,75] However, whereas Na^+Cl^- behave as genuine ionic-bond (colligative properties and conductivity in molten states), the Si^+X^- bonds behave as "sticky bonds". This stickiness originates in the combined contributions of RE_{CS} and the large electrostatic stabilization of the Si+ X− ion-pair. *Both contributions are optimized along the Si—X axis, and make these bonds very strong.*

Si-X vs. C-X Bonds: Comparison of Si-X to C-X bonds[75,76] reveals that while all Si-X bonds are more ionic than the corresponding C-X bonds, nevertheless, these are the C-X bonds that exhibit ionic chemistry in condensed phases whereas the ionic Si-X chemistry is extremely rare.[76]

For example, despite the virtually identical solvation energies, computed[41] for silicenium ions and carbocations, the Si-X bonds avoid heterolysis in solution.[41] In fact, Si-X compounds undergo much faster nucleophilic substitution through pentacoordinated intermediates[77] In contrast, C-X bonds proceed by the classical S_N1 heterolysis followed by recombination of the carbocation with a nucleophile.

Indeed, our recent VB study showed[41] that, unlike the facile heterolysis of Me_3C-Cl (to Me_3C^+ and Cl− ions), the Me_3Si-Cl analog has a very high heterolytic-barrier in water solutions. Thus, whereas Me_3C-Cl has a flat Me_3C^+--- Cl− energy-curve,[41] the corresponding Me_3Si-Cl molecule features in water a $Me_3Si^+Cl^-$ structure in a deep minimum and an almost degenerate covalent Me_3Si•—•Cl structure. As a result of the short Si^+Cl^- distance (~2.3Å), the covalent-ionic mixing is strong leading to a large RE_{CS} stabilization energy (62 kcal·mol⁻¹).[41] Hence, the "Me_3Si---Cl" intermediate in solution, is in fact a CBS, residing in a deep energy-minimum. As such, the Si-Cl barrier to heterolysis in aqueous solution is 62 kcal·mol⁻¹ (50.2 with thermal corrections), *and is entirely due to the loss of the charge-shift resonance energy.*[41] This is why silicon compounds prefer substitution, via penta-coordinated intermediates,[77] over the classical S_N1 mechanism.

These differences carry over to the solid state. Thus, trityl perchlorate is an ionic solid, $Ph_3C^+ClO_4^-$, much like Na^+Cl^-,[76c] and even $^tBu^+$ was bottled.[76d] In contrast, the silicon analog is a molecular solid, consisting of Ph_3Si-$OClO_3$ molecules, having a short Si-O bond.[76e] The RE_{CS} contribution [~46 kcal mol⁻¹ (see Table S1)] to the bond-energy makes the Si-O bond sticky. At the same time, the high positive charge concentrated on Si makes the electrostatic stabilization of the ion-pair **strictly directed along the $(CH_3)_3Si^+$----−$O(ClO_3)$ axis**, keeping as such the $(O_3Cl)O^-$ anion stuck close to the Si+ and away from the negatively charged

CH₃ substituents on Si (see Figure 7). Taken together, all these factors prevent the formation of a three-dimensional lattice of $(CH_3)_3Si^+$ and ClO_4^- ions. By contrast, the corresponding Ph₃C-OClO₃ bond heterolyzes in the solid state to Ph_3C^+ and ClO_4^- ions, since the delocalized positive charge in Ph_3C^+ (see $(CH_3)_3C^+$ in Figure 7) enables the carbocation to benefit from three-dimensional electrostatic interactions in an ionic lattice.

9.4. Articulation of the Potential Catalytic Role of Charge-Shift Resonance

In a recent study, Poranne and Chen investigated C-N bonds in protonated and methylated ammonium-ions, $R_3C-NR'_3^+$, which were prepared in the lab.[78] Using VB and MO calculations, they verified that these (C-N)⁺ bonds are CSBs, with significant RE_{CS}, which exceed ~50 kcal·mol⁻¹. However, they went one step forward, and determined the %RE_{CS} profiles along the C-N bond-lengths, showing that the magnitude of RE_{CS} increases as the C-N distance lengthens and reaches the crossover-point of the "ionic" (C⁺ :N) and "covalent" (C˙ ˙N⁺) VB structures. This is shown for ᵗBu-NH₃⁺ on the left-hand side of Figure 15.
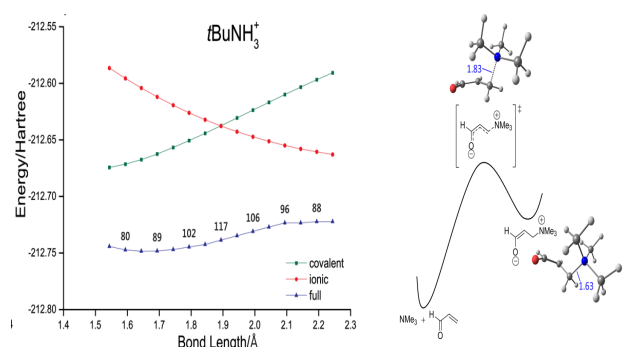

Figure 15. Left: Behavior of red the "ionic" (C⁺ :N) and green "covalent" (C˙ ˙N+) VB structures of tBu-NMe₃⁺, and the variation of the %RE_{CS} character (lowest curve), along the C—N distance. Right: a schematic-plot of a reaction wherein RE_{CS} serves a potential catalytic-role. Adapted from Figures 6d and 8 in Ref. 78, with permission of Wiley-VCH.

Based on these plots, the authors predicted that these long-bond distances are close to the distances in the transition states of nucleophilic Michael addition of nitrogen bases (right-hand side of Figure 15), in which the stretched C-N bond at the transition state should display very large CS character, and lead thereby to catalysis of the reaction. They further noted that the importance of such reactions was emphasized by other groups.[79,80] Another articulation was made by Patil et al[81] who showed that the trends in the key physico-chemical properties of ionic liquids are correlated to the CS character of the protonated N-H bond.

It is yet too early to assess the impact of these articulations. Nevertheless, it is clear that the acceptance of the CSB concept,

would eventually be determined by such articulations by the experimental community.[82]

10. How Do We Define a New Class of Bonding?

The prerequisites for legitimately defining a group of bonds as a new class of bonding should be the affirmative answers to the following key questions:

(i) Do the bonds belonging to the new class have clearly different features than those bonds which belongs to formerly defined classes?

(ii) Is the definition of the new class useful, and does it stimulate chemists to make new predictions?

The foregoing discussions suggest that the answer to both questions is "yes". CSB emerges as a unique category, distinct from covalent/polar-covalent bonds, and certainly from ionic-bonds. As argued in the introduction, the current paradigm of covalent- and ionic-bonds had initially been derived based on empirical behaviors of nonpolar vs. polar substances, in the emerging subfields (organic and inorganic) of chemistry.[5,6,9] It was subsequently rationalized by Pauling, using empirical VB-theory, which resulted in overlooking the CSB family due to the inaccurate assumption that $RE_{CS}(X-X) = 0$.[14c]

As the present essay shows, however, the new CSB family was derived here from ab-initio VB- and MO-theories,[21,22] then confirmed[23] using EDA-DFT, and further characterized by electron density analyses, independent of computational methods.[25,26,28,83] Thus, this property of the new CSB group also appears invariant to the nature of theory used to examine these bonds.

Does the CSB-concept stimulate new predictions and research? Yes indeed. We showed a few experimental manifestations of CSB, including the articulation of the CSB concept,[78] to induce catalysis of reactions which involve nucleophilic attacks by amine, or the relation of the physico-chemical properties of ionic-liquids to the CS character of the protonated N-H bond.[81] As such, the concept certainly appears to stimulate chemists. It also stimulates the electron-density communities of experimentalists and theoreticians who are able to characterise bonds from experimental or theoretic charge densities.[25-28, 52, 54-63, 88]

The key quantity that distinguishes CSBs is the corresponding resonance-energy, RE_{CS}, which is large in CSBs but rather small in covalent- and ionic-bonds. RE_{CS} was quantified from differences of activation energies of halogen vs. hydrogen exchange-reactions[70-72] (other reactions may serve to quantify the RE_{CS} of the respective bonds that undergo activation). The advent of RE_{CS} is important in the same sense as is the RE of

benzene and related conjugated molecules. It seems to us that the *weight of evidence meets the necessary conditions to declare CSB as a distinct family of bonding based on electron-sharing*.

Of course, opposite points of view have appeared and suggested that: (a) CSBs are merely covalent-bonds, which exhibit orbital-shrinkage and kinetic-energy-lowering in the bonding region as in H-H[84], and (b) that positive Laplacians simply typify long covalent bonds, and hence, the long F-F bond is merely a stretched covalent-bond, having a positive Laplacian; and the same should be displayed if we were to stretch H-H.[64] However, we showed that these objections are not firmly founded:

Thus, the statement that the both CSBs and covalent establish bonding by orbital-shrinkage[84] is not supported by computational evidence (Figure 6). In fact, while the orbital-shrinkage is indeed the primary mechanism of bonding for classical covalent bonds as H-H[84] or H_3C-CH_3, it is not so for CSBs (e.g., Cl-Cl, O-O, F-F; see Figure 6) wherein orbital-shrinkage plays a minor role. Hence, CSBs and covalent bonds display fundamental difference in their bonding mechanisms.

Similarly, were F-F simply like the stretched H-H covalent bond,[64] the weights of its ionic structures would have been quite low; but quite to the contrary, one finds that the ionic structures of F_2 have larger weights than those of H_2 (see Table S3). Further, the Laplacians of H-H and F-F are very different across the bond distances (Fig. 12), and the behavior of *the Laplacian of the latter bond is entirely dominated by the charge-shift resonance energy of this bond*.

As such, CSBs and covalent bonds are different bond-types. And both objections[64,84] do not form a particularly useful basis for understanding the features of CSBs that are discussed in this essay.

Of course, one could be tempted to adopt a strict reductionist view which, for the sake of minimizing the number of bond types, would ignore the specific features of CSBs and incorporate these bonds into one vast category of covalent- and polar-covalent-bonds.[84] However, by ignoring the above detailed differences between covalent-bonds and CSBs, this strict reductionist view would have missed the essence from whichever way one examines the data. Thus, whereas H-H would exist without the RE_{CS} increment, the F-F would not. Similarly, without RE_{CS}, most dative-bonds and coordinative-bonds would not have existed, and Si-Cl would have heterolyzed in condensed phases much like C-Cl bonds. Indeed, were the Si-Cl bond just a regular polar-bond, in-between C-Cl and Na-Cl (due to electronegativity differences), there would be a continuity of properties in the series $(CH_3)_3C$-Cl, $(CH_3)_3Si$-Cl, Na-Cl, and $(CH_3)_3Si$-Cl would have readily heterolyzed in water, leading to free silicenium ions. *This is not the case.* Besides, if all nonionic electron-pair bonds were

to be classified in a single category of covalent- and polar-covalent-bonds, the Rundle-Pimentel rationalization of hypervalency would have led to a unified conclusion that all 3-center-4-electron systems would ße stable. *They are not!*

Turning now to barriers of radical exchange reactions, if the covalent-ionic resonance-energy were not exceptionally large in the H-F bond, the energy barriers for the $F^{\cdot}$ + H-F' → F-H + $^{\cdot}F'$ and $H^{\cdot}$ + F-H' → H-F + $^{\cdot}H'$ reactions would have been of the same order of magnitude. The facts are that these barriers are widely different, and the second reaction possesses an astonishingly large barrier due to the diminished RE_{CS} in the corresponding transition state.[72]

These examples and many others show that applying a strict reductionist view, and lumping covalent bonds and CSBs as a single group of "covalent" bonds, would have no advantage for understanding the chemical patterns discussed above, would have lost the predictive-power of the CSB-concept, and on the contrary would be restricted to models that have many exceptions (e.g., Rundle-Pimentel's).

When essential differences are being ignored or brushed away for the sake of reductionism, this deprives chemistry of its diversity and predictivism.[85, 86] On the contrary, defining the CSB category, which gathers and rationalizes many unusual features, enriches chemistry since it allows one to make new predictions regarding molecular structures and reactivity.[72,76f, 78,81,82] Some articulations of the CSB concept that were discussed above attest to the beginning of such process.[78,81] The distinction between covalent-bonds and CSBs is thus, fundamental, and it contributes to useful chemical diversity. As beautifully expressed by Chen et al,[86] "*… the value of the heuristic is judged by the degree to which it is explanatory, and furthermore, predictive of molecular properties*"

The recent activity is indicative that the CSB concept is already stimulating chemists, through articulations of the concept by experimental chemists,[78,81,82] and through QTAIM and ELF analyses of experimental electron-densities, isodesmic-reaction tests,[52,54,55,58,59,87-90] and explorations of how protonation of heteroatoms change their bonds to CSBs,[91] of inverted Si-Si CSBs in silabicyclo[1.1.0]butanes,[92] as well as by predictions of novel helium-bonds,[57] which reveal CSB characteristics. Since the chemical-bond is the heartland of chemistry,[1] we might expect this trend to continue…

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ESSAY

Text for Table of Contents

The vertices of the triangle symbolize the three valence-bond variables/elements, out of which there emerge families of electron-pair bonds
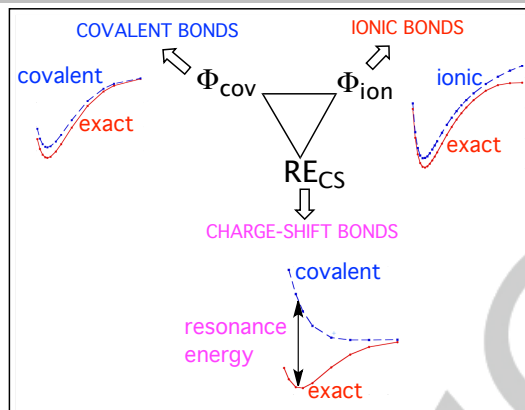
Sason Shaik*, David Danovich, John Morrison Galbright, Benoît Braïda, Wei Wu, and Philippe C. Hiberty*

Charge-Shift Bonding: A New and Unique Form of Bonding.