Charge-Shift Bonding Emerges as a Distinct Electron-Pair Bonding Family from Both Valence Bond and Molecular Orbital Theories

Huaiyu Zhang,[†] David Danovich,[⊥] Wei Wu,*[,†] Benoît Braïda,[‡,∥] Philippe C. Hiberty,*[,§] and Sason Shaik*[,⊥]

[†]The State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, China

[‡]Sorbonne Universités, UPMC Univ Paris 06, UMR 7616, LCT, F-75005, Paris, France

[∥]CNRS, UMR 7616, LCT, F-75005, Paris, France

[§]Laboratoire de Chimie Physique, Groupe de Chimie Théorique, Université de Paris-Sud, CNRS UMR 8000, 91405 Orsay, France

[⊥]Institute of Chemistry and The Lise Meitner-Minerva Center for Computational Quantum Chemistry, The Hebrew University, Jerusalem 91904, Israel

S *Supporting Information*

ABSTRACT: The charge-shift bonding (CSB) concept was originally discovered through valence bond (VB) calculations. Later, CSB was found to have signatures in atoms-in-molecules and electron-localization-function and in experimental electron density measurements. However, the CSB concept has never been derived from a molecular orbital (MO)-based theory. We now provide a proof of principle that an MO-based approach enables one to derive the CSB family alongside the distinctly different classical family of covalent bonds. In this bridging energy decomposition analysis, the covalent–ionic resonance

energy, RE_{CS}, of a bond is extracted by cloning an MO-based purely covalent reference state, which is a constrained two-configuration wave function. The energy gap between this reference state and the variational TCSCF ground state yields numerical values for RE_{CS}, which correlate with the values obtained at the VBSCF level. This simple MO-based method, which only takes care of static electron correlation, is already sufficient for distinguishing the classical covalent or polar-covalent bonds from charge-shift bonds. The equivalence of the VB and MO-based methods is further demonstrated when both methods are augmented by dynamic correlation. Thus, it is shown from both MO and VB perspectives that the bonding in the CSB family does not arise from electron correlation. Considering that the existence of the CSB family is associated also with quite a few experimental observations that we already reviewed (Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. *Nat. Chem.*, **2009**, *1*, 443−449), the new bonding concept has passed by now two stringent tests. This derivation, on the one hand, supports the new concept and on the other, it creates bridges between the two main theories of electronic structure.
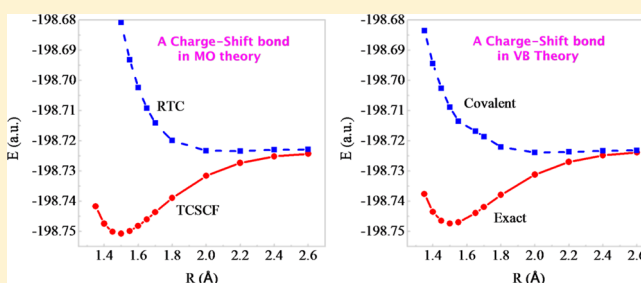
INTRODUCTION

To be widely acceptable, a new concept must pass some essential tests. It should be predictive and/or a successful interpreter of experimental data. And it should be derivable from all available theoretical frames, and be independent of the theory that is used to derive it, at least in a clear qualitative sense. The concept we wish to put herein into this last test is the existence of a distinct family of electron-pair bonds, the so-called charge-shift bonding (CSB) concept.[1] The CSB concept originated in valence bond (VB) theory,[2,3] and although it found clear signatures in other theoretical approaches like atoms-in-molecules (AIM) and electron-localization-function (ELF) and was linked to experimental findings,[1,4−6] what is definitely missing is the derivation of CSB from the all important and popular molecular orbital (MO) theory. Such a derivation will not only support the concept but also create

bridges between the two important chemical theories of electronic structure.

Three Families of Electron-Pair Bonding. The charge-shift bonding concept originated from early VB calculations,[2,3] which showed that along with the classical electron-pair bond families, the covalent and the ionic ones, there exists a third and distinct family of bonds. These three bond families are illustrated in Scheme 1 using the three VB structures that are needed to describe electron pair bonding in a generic A−X bond. The covalent structure, **1** in Scheme 1a, is the major descriptor of polar-covalent bonds, and its binding energy (D_{cov}) derives from the spin-exchange resonance energy between the two spin arrangement patterns of the structure.[4,7]

Scheme 1. Covalent and Ionic Structures of an Electron-Pair Bond between A and X^a
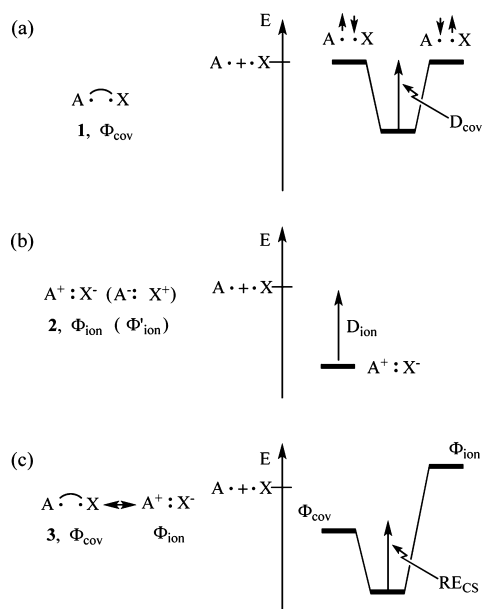
^{a}(a) The covalent structure **1**, Φ_{cov}. The arched line connecting the two electrons signifies singlet pairing of the electrons. The spin-pairing results in the covalent bond energy, D_{cov}, due to the mixing of the two spin arrangement patterns needed to create a singlet pair. This is the dominant contribution to bonding in the family of covalent bonds. (b) The ionic structures **2**, Φ_{ion} and Φ'_{ion}, and the Coulomb stabilization energy relative to the separated atoms, D_{ion}. D_{ion} is the dominant contribution to bonding in the family of ionic bonds. (c) The resonance, **3**, between the covalent and ionic structures of the bond, and the charge-shift resonance energy, RE_{CS}, due to this mixing. The RE_{CS} quantity constitutes the main bonding component of charge-shift bonding.

For bonds like H−H, C−H, Li−Li, C−Cl, Si−Si, Si−H, etc., the bond energy is dominated by the D_{cov} spin-pairing energy.[1] These are classical covalent bonds.

The second classical family consists of ionic bonds wherein the main bond descriptor is one of the ionic structures, shown in **2**, Scheme 1b. In these bonds, the ionic structure lies well below the separate atoms, and the bond energy is dominated by the Coulomb stabilization energy (D_{ion}) of the opposite charges in the ionic structure, e.g., A$^+$:X$^−$. Bonds like NaCl, NaF, and LiF, which were computed by VB theory, belong to the ionic bond family.[1]

In the third family that was discovered through the VB calculations,[2,3] the bonding energy does not reflect neither the spin-pairing stabilization of the covalent structure nor the Coulomb stabilization energy due to the ionic structure; both VB structures are either unbound relative to the separated atoms, or only weakly so. In these bonds, most or all of the bonding energy arises due to the resonance energy, RE_{CS}, between the covalent and the ionic structures of the electron pair bond, **3** in Scheme 1c. We call this bonding type charge-shift bonding (CSB), because it arises from the covalent−ionic fluctuation of the electron pair. Some of the bonds which belong to the CSB family are F−F, O−O, H−F, and C−F,[1] the bonding in hyper-coordinated molecules such as F−Xe−F,[8] etc.

To exemplify the VB results that led to the initial recognition of the CSB family, we show in Figure 1 two prototypical electron pair bonds of the homonuclear molecules H$_2$ and F$_2$. It
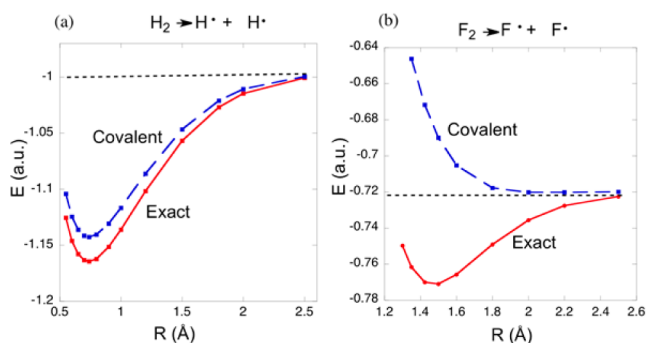

Figure 1. Dissociation energy curves for (a) H$_2$ and (b) F$_2$. The blue lines with squares show the purely covalent VB structures. Red lines with squares show the optimized covalent + ionic "exact" ground state. Reproduced from ref 1. with permission from Nature Chemistry.

is seen that in H$_2$ the covalent structure, H·−·H, is nicely stabilized and it has an energy minimum that coincides with the full energy curve both in terms of distance and energy. The mixing of the two ionic structures, H$^+$:H$^−$ and H:$^−$H$^+$, into the covalent structure makes obviously a marginal contribution to the bond energy. By contrast, in F$_2$ the covalent structure, F·−·F, is repulsive throughout the interatomic distance, and it is the mixing with the higher lying ionic structures, F$^+$:F$^−$ and F:$^−$ F$^+$, that generates the minimum with a significant bonding energy (red curve). Clearly, here, is not only that the stabilization brought by the ionic structures is far from being marginal but it is in fact decisive in creating the bond energy between the two fluorine atoms. Thus, according to VB theory, the bonding in F$_2$ owes its origins to the charge-shift resonance energy between the covalent and ionic states of the bond (as in **3** in Scheme 1c), even though the bond has no static ionicity.

In the course of time since 1991, we have found many bonds that follow the same pattern and are therefore CSB. We have shown that the CSB family can be reasoned based on the virial theorem,[1,2,9] to arise from the requirement to restore the virial ratio ($T/V = −1/2$) between the kinetic (T) and potential (V) electron energies, and establish a bond at equilibrium. This restoration is required in response to the rise in the kinetic energy of the electrons due to shrinkage of the atoms during bonding and the Pauli repulsion exerted on the bonding electrons by lone pairs having the same symmetry, as the σ-type lone pairs in F−F. We further noted that CSBs have specific signatures in electron density analyses, such as atoms-in-molecules (AIM),[10] and electron-localization-function (ELF) theory.[11] Finally, we found experimental manifestations of CS-bonding, and we even showed that the RE_{CS} quantity is quantifiable from experiments in some cases.[1,12−14]

However, the derivation of CSB from MO-based theory has not been achieved yet. Besides, as in a molecule like F$_2$, where any bonding interaction is retrieved within MO theory only after extensive configuration interaction, it is tempting to consider CSB as bonds "arising from electronic correlation", and to either view CSB as some curiosity of VB theory, or even to view the correlation energy as a measure of the CS character of a bond. Following our definition of a widely acceptable concept, we now put CSB into a stringent test, with the aim of answering two questions: (i) can CSB be derived from MO theory and (ii) is CSB really due to electron correlation? As shall be seen the answers are, yes and no, respectively.

DERIVING CSB FROM MO THEORY

The key ingredient needed for deriving RE_{CS} quantities for CSBs and/or covalent bonds from MO-based theory is a reference state that qualifies as the covalent structure, which is the lowest energy structure in correlated MO-based wave functions. Using this reference, one could then obtain the RE_{CS} property of the bond from a correlated MO-based wave function that contains also the ionic forms. This would be an MO-based energy decomposition analysis, geared toward giving results compatible with VB theory.

Let us first demonstrate that the RE_{CS} quantity can indeed be extracted from an MO-based approach for H—H and F—F. This derivation will provide us sufficient insight into addressing the common wisdom that "F_2 is bonded by correlation". Furthermore, the derivation will enable us to discuss the actual origins of the bond according to the emerging picture from both VB and MO-based theories. We shall then show how one can systematically obtain this quantity, for homonuclear and heteronuclear bonds, and derive the existence of the CSB family from a correlated MO-based approach. The clearest picture can be obtained from a two-configuration self-consistent-field (TCSCF) wave function, which includes static correlation of the electron pair, and can be easily mapped into a VB language. Subsequently, we shall address the role of dynamic correlation within VB and MO theories.

DERIVATION OF RE_{CS} FOR THE H—H BOND USING ORBITAL-OPTIMIZED TWO-CONFIGURATION REFERENCE STATE

Consider two atoms, A and B, linked by a simple homonuclear bond, which in a minimal orbital basis set, possess a pair of orbitals, bonding and antibonding, as depicted in Scheme 2, and labeled for convenience as ϕ and ϕ^*, respectively.

Scheme 2. Schematic Representations of the Bonding and Antibonding Orbitals, ϕ and ϕ^*, for a Homonuclear Bond, and the Fundamental and Diexcited MO Configurations
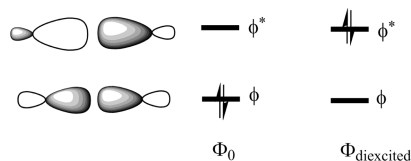
These orbitals are defined most generally in eqs 1a and 1b:

$$\phi = N(\varphi_a + \varphi_b) \tag{1a}$$

$$\phi^* = N'(\varphi'_a - \varphi'_b) \tag{1b}$$

Here N and N' are normalization constants, and φ_a/φ_b and φ'_a/φ'_b are the hybrid atomic orbitals (HAOs) on the two centers of the bond. In any extended basis set, φ_a/φ_b are different than φ'_a/φ'_b, and $N \neq N'$. If these were Hückel type orbitals, then φ_a/φ_b would be identical to φ'_a/φ'_b and we would have $N = N' = 2^{-1/2}$. With Hückel type orbitals, it is very simple to define an MO-based reference state that will be identical to the covalent structure in VB theory. This is the reference two-configuration (RTC) wave function, Ψ_{RTC}, which mixes the ground and diexcited configurations with equal coefficients, as shown in eq 2:

$$\Psi_{RTC}(\text{Hückel−MOs})$$
$$= 2^{-1/2}[|\phi\bar{\phi}| - |\phi^*\bar{\phi}^*|]$$
$$= 2^{-1/2}[|\varphi_a\bar{\varphi}_b| - |\bar{\varphi}_a\varphi_b|]$$
$$= \Phi_{cov} \tag{2}$$

Here it can be easily seen that the ionic terms cancel out after expanding ϕ and ϕ^* in terms of the HAOs φ_a and φ_b, and thus expanding $|\phi\bar{\phi}|$ and $|\phi^*\bar{\phi}^*|$ in terms of VB structures.[7] However, because we are not dealing with Hückel orbitals we cannot apply eq 2 as is. Nevertheless, one can use the general form of the wave function in eq 3, where ϕ is a bonding orbital, and ϕ'^* is a virtual orbital composed of the same HAOs φ_a and φ_b as in the bonding orbital, even in an extended basis set:

$$\Psi_{RTC} = C_{RTC}|\phi\bar{\phi}| - C'_{RTC}|\phi'^*\bar{\phi}'^*|$$
$$\text{where } \phi = N(\varphi_a + \varphi_b) \quad \text{and } \phi'^* = N'(\varphi_a - \varphi_b) \tag{3}$$

We then determine C_{RTC} and C'_{RTC} by imposing, along with the normalization condition of the wave function, the following constraints:

$$\frac{C_{RTC}}{C'_{RTC}} = \frac{N'^2}{N^2}$$

$$\text{where } N = \left[\frac{1}{2(1 + S_{ab})}\right]^{-1/2} \text{ and } N' = \left[\frac{1}{2(1 - S_{ab})}\right]^{-1/2} \tag{4}$$

Here S_{ab} is the overlap of the two hybrid atomic orbitals on atoms A and B.

Using eqs 3 and 4, one precisely obtains the desired reference state:

$$\Psi_{RTC} = \tilde{N}_{RTC}(|\tilde{\phi}\bar{\tilde{\phi}}| - |\tilde{\phi}'^*\bar{\tilde{\phi}}'^*|) = \Phi_{cov} \tag{5}$$

where $\tilde{N}_{RTC} = C_{RTC} \times N^2 = C'_{RTC} \times N'^2$, and $\tilde{\phi}/\tilde{\phi}'^*$ are the non-normalized orbitals $(\varphi_a + \varphi_b)$ and $(\varphi_a - \varphi_b)$, respectively.

Subsequently, these φ_a and φ_b HAOs could be optimized following the variational principle, leading for H_2 to an MO-based wave function Ψ_{RTC} that is identical to the purely covalent VB structure, which is routinely provided by any nonorthogonal VB code.

As is well-known, the VBSCF wave function with three structures, one covalent and two ionic, is equivalent to the TCSCF wave function. Consequently, in a second calculation, we represent the VBSCF wave function in the MO-based scheme, by the variational TCSCF wave function without any constraints on the coefficients, other than requiring Ψ_{TCSCF} to be normalized:

$$\Psi_{TCSCF} = C|\phi\bar{\phi}| - (1 - C^2)^{1/2}|\phi^*\bar{\phi}^*| \tag{6}$$

Having the two wave functions in eqs 5 and 6, the RE_{CS} quantity is most simply calculated in eq 7 as the energy difference between the ground state Ψ_{TCSCF} and the covalent reference Ψ_{RTC}:

$$RE_{CS} = E(\Psi_{RTC}) - E(\Psi_{TCSCF}) \tag{7}$$

Using eqs 3−7, and doing the calculations for three different basis sets: STO-3G, 6-31G, and 6-31G**, we obtained the following RE_{CS} values: 8.15, 5.85, and 4.31 kcal mol^{-1}, respectively. The corresponding valence bond self-consistent field (VBSCF) values using the same basis sets are virtually identical (see the Supporting Information).

It is also possible to plot the energy curves for the variational TCSCF ground state and for the reference RTC covalent state. The so-generated energy curves are shown in Figure 2a, along
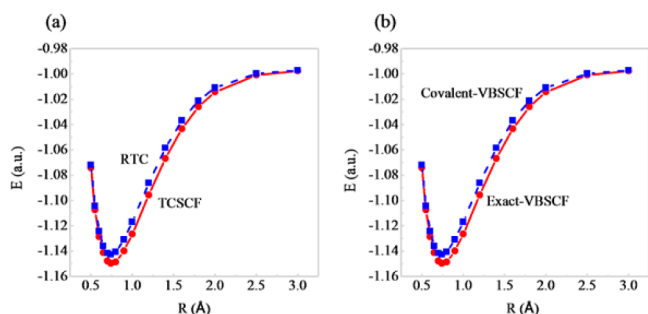

Figure 2. Energy curves of the covalent structure (blue squares) and the variational wave function (red circles) of the H−H bond using the 6-31G** basis set: (a) Using the MO based reference state (Ψ_{RTC} in eq 5) and the variational TCSCF curves, (b) using VBSCF calculations for the covalent and full bond wave functions.

with the corresponding covalent and ground state VBSCF curves in Figure 2b. In both cases, we see that the covalent curve (blue curves and squares), whether calculated within MO theory (Ψ_{RTC}, Figure 2a) or VB theory (covalent-VBSCF, Figure 2b), is close but not identical to the corresponding full ground state (red curves and circles), as expected for H_2 where the bond energy is dominated by the spin-pairing energy of the covalent bond, while the RE_{CS} quantity is small.

Importantly, it clearly appears that the Ψ_{RTC} covalent reference in Figure 2a is identical to the VB-calculated covalent structure in Figure 2b, as shown in eq 5. Furthermore, at the same time, the variational TCSCF curve for the ground state in Figure 2a matches the full-VBSCF curve in Figure 2b (red circles) very well. Thus, it is apparent that the MO-based results in Figure 2a are identical to the VB results in Figure 2b, and that, in both cases, the RE_{CS} is a small fraction of the calculated bond energy (4.5% using the 6-31G** basis set). This provides a proof of principle that the covalent−ionic resonance energy, RE_{CS}, of a bond can be extracted from MO theory using an MO-based reference state.

■ DERIVATION OF THE RE_{CS} QUANTITY FOR THE F−F BOND USING THE RTC/TCSCF WAVE FUNCTIONS

The MO derivation of the variational TCSCF wave function and the reference two configuration (RTC) state for a general A−X bond in a polyelectronic molecule, can be done by generalizing eqs 3 and 6 to eqs 8a and 8b, wherein θ is a generic term representing the set of inactive MOs not involved in the bond being studied.

$$\Psi_{RTC} = C_{RTC}|...\theta\bar{\theta}...\phi\bar{\phi}| - C'_{RTC}|..\theta\bar{\theta}...\phi'*\bar{\phi}'*| \quad (8a)$$

$$\Psi_{TCSCF} = C|...\theta\bar{\theta}...\phi\bar{\phi}| - (1-C^2)^{1/2}|..\theta\bar{\theta}...\phi*\bar{\phi}*| \quad (8b)$$

Using eq 8a with orbital optimization becomes cumbersome in the general case, as some technical difficulties are encountered with the optimization of the inactive orbitals of the wave function.[15] It is possible, however, to define a widely valid reference wave function Ψ_{RTC} that is easily computable by means of the following procedure: (i) use in eq 8a the bonding MO ϕ and the inactive MOs θ as they are in the variational TCSCF wave function of eq 8b. (ii) Construct an antibonding

MO $\phi'*$ using the same HAOs φ_a and φ_b as in ϕ. (iii) Impose the same polarity in $\phi'*$ as in ϕ, as shown in eq 9:

$$\phi = N(\varphi_a + \lambda\varphi_b) \quad \text{and} \quad \phi'* = N'(\varphi_a - \lambda\varphi_b) \quad (9)$$

Finally, in step (iv) we calculate the C_{RTC} and C'_{RTC} coefficients (eq 8a) by means of eq 4.

Expansion of this Ψ_{RTC} in terms of VB structures (as was done above for H_2) shows that the ionic components cancel out for any λ value, and there remains only the pure covalent VB structure. Subsequent calculations of the variational TCSCF energy will provide us the RE_{CS} quantities for any bond, based on eq 7. For homonuclear molecules, $\lambda = 1$.

Note that at this simple MO-based computational level, which in principle is nearly equivalent to the VBSCF level, only the static electron correlation is taken into account for the ground state curve. Nevertheless, at the moment, this is of no concern, because we want to demonstrate the equivalence of MO(RTC/TCSCF) and VB(covalent/full-VBSCF). In a subsequent section, we shall show that the same MO-VB equivalence exists at the level of dynamic correlation, which in turn brings about more accurate RE_{CS} and bonding energies.

Figure 3a shows a plot of the energy curves for the Ψ_{RTC} and Ψ_{TCSCF} states of the F−F bond using the 6-31G* basis sets
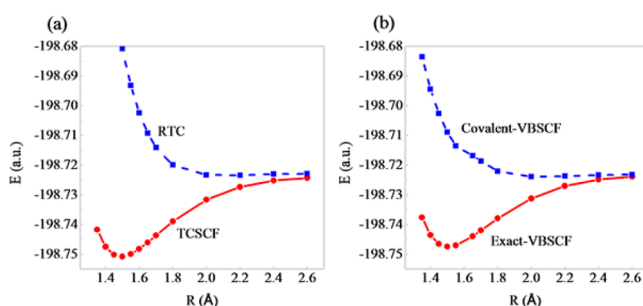

Figure 3. Energy curves for F−F using 6-31G*. (a) The blue curve is the two-configuration (RTC) reference state, whereas the red curve is the variational TCSCF curve. (b) The corresponding covalent and full VBSCF curves.

(identical ones are obtained for 6-31G and 6-31+G*). Figure 3b shows the covalent and full ground state curves generated by VBSCF/6-31G* calculations. It is seen that the energy curves in Figures 3a,b have virtually identical appearances, and are similar to those obtained by the higher-level VB calculations in Figure 1b. The most prominent feature in Figure 3 is the purely repulsive covalent curve, such that the bonding energy arises only from the RE_{CS} due to the mixing of the ionic structures into the covalent structure or the reference state.

A comparison of the MO-based two-configuration calculations of F_2 (Figure 3a) to H_2 (Figure 2a) shows that the $RE_{CS}(F_2)$ is an order of magnitude larger than the $RE_{CS}(H_2)$ quantity. Furthermore, although for the H−H bond the RE_{CS} quantity is much smaller than the corresponding bond dissociation energy (BDE), the situation is precisely the opposite for the F−F bond. For F−F, RE_{CS} is much larger than the 6-31G* computed BDE (it is larger also than the experimental BDE), such that the RE_{CS} is entirely responsible for bonding, and the RE_{CS}/BDE ratio is much larger than 1. Thus, both VB and the MO-based TCSCF calculations exhibit the same dichotomy for the H_2 and F_2 bonds, one being covalent and the other being bonded by charge-shift bonding (CSB). As such, our result constitutes a proof of principle that

the two bond types can be distinguished from MO-based theory using an MO-based reference state.

GENERALIZATION OF ELECTRON PAIR BONDING FAMILIES FROM MO-BASED WAVE FUNCTIONS

As mentioned above, eqs 8a, 8b, and 9 hold for F−F, as well as for other homonuclear and heteronuclear bonds. Table 1 shows

Table 1. RE_{CS} Values (in kcal mol^{-1}) Computed with the "TCSCF Approach" and the VBSCF Method Using 6-31G* and Corresponding %RE_{CS} Values

	RTC/TCSCF		VBSCF		
bond/molecule[a]	RE_{CS}[b]	%RE_{CS}[c]	RE_{CS}	%RE_{CS}[c]	χ_{av}[d]
H−H/H$_2$	5.9	6.6	5.9	6.6	2.20
C−C/C$_2$H$_6$	26.3	31.2	14.1	16.9	2.55
N−N/N$_2$H$_4$	51.9	97.6	32.7	62.4	3.04
O−O/H$_2$O$_2$	51.4	165.4	42.2	147.4	3.44
F−F/F$_2$	46.4	297.5	41.6	321.2	3.98
C−H/CH$_4$	15.1	15.2	11.9	12.1	2.38
H−F/HF	109.4	104.4	90.7	88.6	3.09

[a]CCSD(T)/aug-cc-pVQZ optimized geometries for H$_2$, H$_2$O$_2$, and F$_2$, and MP2/aug-cc-pVQZ optimized geometries for other molecules. [b]See eqs 3−4 and 8a and 8b. [c]%RE_{CS} = 100 × (RE_{CS}/BDE). [d]This is the average electronegativity χ_{av} = 1/2 $[\chi_A + \chi_X]$ where A and X are the constituents of the bond A−X.

the TCSCF analysis for seven homo- and heteronuclear bonds, along with the corresponding VBSCF results and the average electronegativity of the bond constituents, χ_{av}. It can be seen that the RE_{CS} values calculated by the TCSCF approach are generally larger than those from VBSCF. This is expected as the φ_a and φ_b HAOs are not optimized in Ψ_{RTC} (eq 8a), leading to a covalent reference state that is necessarily somewhat higher that the VBSCF one wherein orbitals are fully optimized. Still, the tendencies for TCSCF and VBSCF are identical. In particular, the %RE_{CS}(TCSCF) values (%RE_{CS} = 100 × (RE_{CS}/BDE)) are very informative. It is seen that H−H, C−H, and C−C bonds possess %RE_{CS} values well below 50% of the corresponding BDEs. By contrast, N−N, O−O, F−F, and H−F exhibit %RE_{CS}(TCSCF) values that are identical or much larger than the corresponding BDE values (>100%). Thus, in these latter bonds, most or the entire BDE arises from the charge-shift resonance energy, and some of these bonds, e.g., F−F and O−O, owe their existence entirely to the charge-shift resonance energy.

Figure 4 displays correlations of the %RE_{CS} quantities. Thus, as shown in Figure 4a, the %RE_{CS}(TCSCF) and %
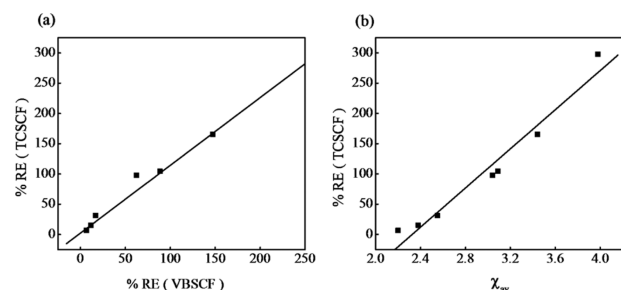
RE_{CS}(VBSCF) values behave alike, and correlate with one another. Furthermore, it was demonstrated before in the VB framework[1,4,16] that the charge-shift character, gauged by % RE_{CS}, correlates with the average electronegativity, χ_{av}, of the bond constituents.

It can be seen in Figure 4b that the correlation still holds when the charge-shift character %RE_{CS}(TCSCF) is derived from MO theory. As the electronegativity of the bonded atoms increases from left to right of the periodic table, so does the % RE_{CS}(TCSCF). Thus, the correlation displayed in Figure 4b confirms that the key physical properties that determine the value of RE_{CS} are the small size of the atom and its lone-pair richness.[1,4] These properties of the atom or fragment increase the kinetic energy of the electrons in the bonding region and require large RE_{CS} values to restore the virial ratio and establish an equilibrium bonding. Identifying the two bonding families in Table 1 therefore provides a proof of principle that the "existence" of the covalent and CSB bond families can be reasoned either from VB theory or from MO theory using an MO-based reference state.

RE_{CS} STABILIZATION ENERGIES DERIVED FROM TCSCF ARE NOT CORRELATION ENERGIES!

The above equivalence of the %RE_{CS} quantities derived from VBSCF and TCSCF, and the general fact that any MO wave function can be mapped into a VB one and vice versa, means that the two theories cannot tell us something that would be physically different about the origin of any bond. Yet, by construction, correlated MO-based methods deal with correlation energy effects on bonding, whereas VB deals with resonance energy effects, and this might be a source of some confusion. Let us elaborate this point a bit.

Thus, in the MO case, the Hartree−Fock (HF) bonding energy has to be corrected by adding the correlation energy difference, ΔE_C, between the separate fragments and the molecule at equilibrium. On the other hand, in VB theory the covalent bonding energy is corrected by the covalent-ionic resonance energy RE_{CS}. This is especially acute for F$_2$, which is devoid of any bonding the HF-MO level as well as at the covalent-VB level. As such, a quick but incorrect reasoning might lead to the conclusion that the ΔE_C and RE_{CS} are more or less one and the same quantity, and that in fact, RE_{CS} is nothing else but some correlation effect. It is not so, and it is therefore important to clarify that the RE_{CS} extracted from the MO calculation is not associated with electron correlation energy.

At the HF level, each electron is considered to be moving in an average field created by the other electrons, and forming an electron-probability cloud without disturbing the positions of the other electrons. This obviously exaggerates the probability of finding two identical spin electrons in the same region of space or opposite-spin electrons in the same HAO, and this is reflected in overestimating the contributions of ionic terms. For example, for a homonuclear bond A−A, the corresponding Ψ_{HF} is 50% ionic, as shown in eq 10, in terms of the respective weights.

$$\Psi_{HF}(A−A) = 50\%(A\cdot{-}\cdot A) + 50\%(A^+ :A^- + A:^- A^+)$$

(10)

Electron correlation restores the relative importance of covalent and ionic structures, by increasing the covalent component and decreasing the ionic one, as in the correlated

Figure 4. (a) Plot of %RE_{CS}(TCSCF) vs %RE_{CS}(VBSCF) for the bonds in Table 1. (b) Plot of %RE_{CS}(TCSCF) vs the average electronegativity of the bond constituents, χ_{av} = 1/2 $[\chi_A + \chi_X]$.

wave function Ψ_{TCSCF} in eq 11, where the quantities λ and $(1 - \lambda)$ are weights of the respective VB structures:

$$\Psi_{TCSCF}(A-A) = (1 - \lambda)(A\cdot-\cdot A)$$
$$+ \lambda(A^+ :A^- + A:^- A^+); \quad \lambda < 0.5 \quad (11)$$

In the VB framework, we start from the covalent reference Φ_{cov} which is 100% covalent (eq 12):

$$\Phi_{cov}(A-A) = 100\%(A\cdot-\cdot A) \quad (12)$$

and subsequently restore some ionicity by the covalent-ionic mixing. In turn, the covalent−ionic mixing decreases the contribution of the covalent component and leads to the optimal covalent−ionic wave function Ψ_{TCSCF}, eq 11. As such, MO and VB start at opposite ends and meet at the same point.

It can be seen, therefore, that the correlation energy ΔE_C results from diminishing the probability of finding two electrons on the same atom to less that 50%, while, on the contrary, the resonance energy RE_{CS} stabilizes the bond and increases this probability from 0% to a finite value. It is therefore clear that ΔE_C and RE_{CS} have completely different physical origins and that CSB is not a manifestation of the electron correlation.

In fact, as we saw in Figures 2, 3, and 4a, the VB and MO descriptions can be brought to complete equivalence, which is schematized in Scheme 3. Thus, the reference state, Ψ_{RTC} (see

Scheme 3. Energy Diagrams Showing the Equivalence of the VB and MO Perspectives[a]
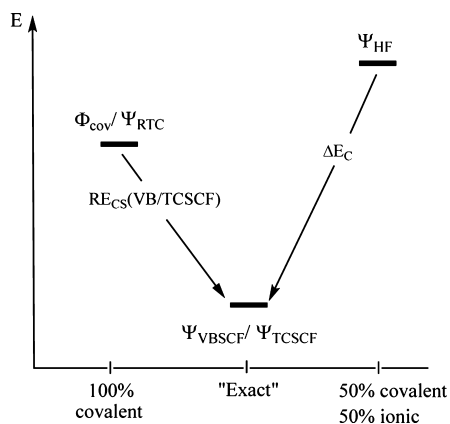
[a]In both cases, the energy difference between the variational and reference states is RE_{CS}. In the MO-perspective we show also Ψ_{HF}, and its correlation energy correction ΔE_C.

eq 8a) is identical with the covalent structure Φ_{cov}, and both represent a wave function in which the electrons keep completely apart; when electron 1 is on atom A, electron 2 is on X, and vice versa. The variational wave functions, Ψ_{VBSCF} in VB, and the MO-based one Ψ_{TCSCF} (eq 8b), are also equivalent and corresponding to optimized mixtures of covalent and ionic structures.[7] Thus, as shown in Scheme 3, in both cases the energy difference between the corresponding variational and the reference states (Φ_{cov} or Ψ_{RTC}) is RE_{CS}, in complete agreement with all the above results. In this sense, both VB theory and the MO-based TCSCF approach provide identical perspectives regarding the origins of bonding.

As further seen in Scheme 3, the common MO-based view that the bonding in F_2 results from electronic correlation is rooted in the use of the single determinant HF wave function

Ψ_{HF} (the first determinant in eq 8b) as a reference state. In this manner, the reference states of MO and VB are different and the emergent roots of bonding necessarily look very different. However, when both theories use the same reference state, both reach the same conclusion about the origins of bonding and the appearance of the CSB family alongside the covalent bond family.

Because one could reverse the argument by using a constrained VB reference state (having now 50% covalent/ionic contributions), one could have of course asked which reference state is more appropriate? We think that the best reference state is the covalent structure in VB and its MO-based Ψ_{RTC} clone, because this reference keeps the same electron distribution as in the separate atoms and does not include an arbitrary and unrealistic electronic reorganization to a 50%−50% covalent−ionic mixture.

ROLE OF DYNAMIC CORRELATION IN THE DESCRIPTION OF BONDING

A. VB Theory. Because the TCSCF state does not include any correction due to dynamic correlation, our above derivation of CSB is associated only with the nondynamic (or static) correlation of the electron pair of the bond. This in turn shows that the "appearance of the CSB family" from a TCSCF wave function does not require any dynamic correlation. However, because lack of dynamic correlation results in rather inaccurate calculated bonding energies (see Table 2, entries 1 and 2) the

Table 2. Bond Energies (D_e), Differential Dynamic Dressing Energies (ΔDDE) and Charge-Shift Resonance Energies (RE_{CS}) for C−C, N−N, O−O, and F−F bonds, from MO-based and VB-based calculations[a]
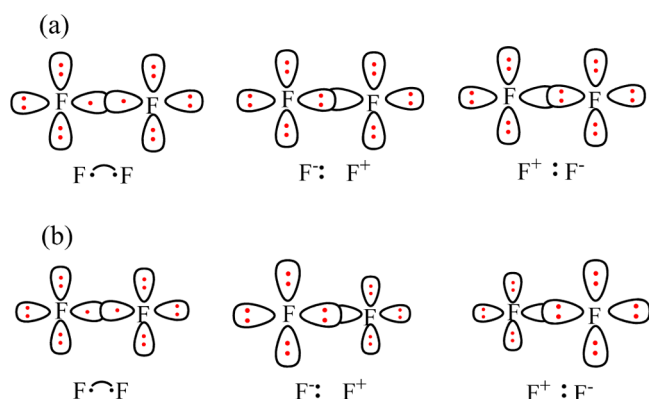
	H_3C-CH_3	H_2N-NH_2	HO−OH	F−F
D_e(VBSCF)	83.3	52.4	28.6	13.0
D_e(TCSCF)	84.2	53.2	31.0	15.6
ΔDDE(MO-based)	13.7	18.5	25.7	25.7
D_e(TCSCF+PT2)	97.9	71.7	56.7	41.3
D_e(BOVB)[b]	94.7	68.5	50.8	36.2
D_e(exp.)	96.7	75.4	53.9	38.3
RE_{CS}(TCSCF+PT2)	40.0	70.4	77.0	72.1
RE_{CS}(BOVB)[b]	28.3	48.9	62.5	66.7
%RE_{CS} (TCSCF+PT2)	40.8	98.2	135.9	174.6
%RE_{CS}(BOVB)[b]	29.9	71.4	123.0	184.3

[a]All energies in kcal/mol. [b]From ref 4.

question we wish to address now is whether the above VB−MO equivalence still holds true after inclusion of dynamical correlation? As shall be seen, the inclusion of dynamic correlation energy does not change the bond classification to covalent and CSB families as found at the above VBSCF and TCSCF levels.

As we have amply shown before,[17−20] one can include dynamic correlation in VB theory while still conserving the set of three VB structures, one covalent and two ionics, which are required to describe an electron pair bond. One of these methods is called breathing orbital VB (BOVB).[17] BOVB allows the three VB structures a freedom of assuming orbital-shapes and sizes that are different for the different structures upon VB mixing. This is illustrated in Scheme 4, which depicts the orbitals for the VB structures of the F−F bond, in BOVB compared with VBSCF, where this freedom does not exist.

Scheme 4. Covalent and Ionic Structures of F−F, and Their Mixing That Leads to RE$_{CS}$ stabilization: (a) in VBSCF and (b) in BOVB

(a)

(b)

Scheme 5. Covalent−Ionic Mixing in the VBSCF and BOVB Three Structure Wave Functions, Where Dynamic Correlation Lowers the Ionic Structures and Enhances the Mixing, Leading to Larger RE$_{CS}$
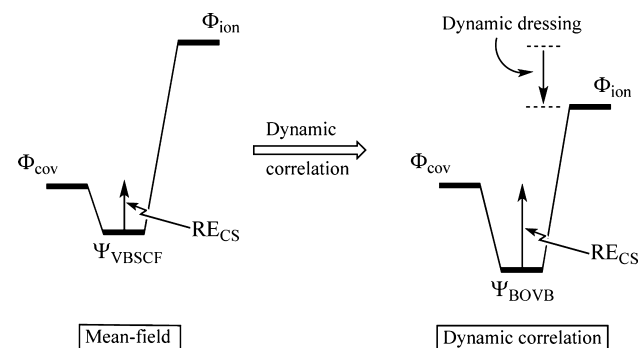

At the VBSCF level (Scheme 4a), the VB structures are constructed out of a common set of orbitals (like in all MCSCF or CASSCF wave functions), which are optimized for an average mean-field situation in which the two atoms are neutral. Such orbitals are appropriate for the covalent structure, but not for either of the ionic structures in which one F atom is cationic while the other is anionic. Thus, in the absence of dynamic correlation at the VBSCF level, the ionic structures are poorly described and therefore they are higher in energy than they should.[21] This results in an underestimated mixing with the covalent structure. Consequently, both the RE$_{CS}$ and the weights of the ionic structures are underestimated, and the resulting bond energy is too small. On the other hand, as shown in Scheme 4b, by allowing different structures to have different orbitals during the optimization of the wave function, BOVB remedies this unfavorable situation by getting rid of the mean-field constraint, and allowing the ionic structures to assume their correct energy levels. As a result, the hybrid atomic orbitals (HAOs) and lone-pair orbitals of the covalent structure assume medium sizes, while ionic structures have more diffuse orbitals on the anionic F:$^−$ species and more compact ones on the cationic F$^+$ species. Thus, in BOVB, *the VB structures are dressed with dynamic correlation*, and the three structures are treated on an equal footing, having orbitals that assume the shapes and sizes needed for optimizing the bonding. Therefore, the lowering of the covalent−ionic energy gap by the dynamic correlation dressing increases the covalent−ionic mixing, and leads to higher RE$_{CS}$ and bonding energy.[22]

Scheme 5 summarizes this information in a pictorial manner. Thus, at the VBSCF level, there is no dynamic correlation and the ionic structures are high. Dressing the VB structures with dynamic correlation does not affect the covalent structure, whereas ionic ones are significantly lowered. The result is an enhanced covalent−ionic mixing and much larger RE$_{CS}$ at the BOVB level. Because the covalent structure is not affected by dynamic correlation, the incremental RE$_{CS}$ (ΔRE$_{CS}$) is simply the difference in the corresponding bond energies, as defined by eq 13:

$$\Delta RE_{CS} = D_e(BOVB) - D_e(VBSCF) \tag{13}$$

Thus, the breathing-orbital effect is nothing else but the instantaneous adaption of the structures to the charge fluctuation of the bond being broken/formed. We call the corresponding energy effect "differential dynamic dressing energy" (ΔDDE), and this quantity is simply calculated in the VB framework through eq 14 for the ΔDDE that is associated with the breaking/formation of a given bond:

$$\Delta DDE(VB\text{-}based) = \Delta RE_{CS} = D_e(BOVB) - D_e(VBSCF) \tag{14}$$

B. MO-based Theory. As has been shown already, the MO-based TCSCF level brings in only static correlation to the electron pair bonding, but it is easy to get dynamic correlation by having this level augmented by a Møller−Plesset perturbative treatment to second order (PT2). Then, in harmony with eq 14, the MO-based value of the ΔDDE associated with a given bond is simply obtained by calculating its dissociation energy first at the TCSCF level, then at the level of TCSCF followed by perturbation:

$$\Delta DDE(MO\text{-}based) = D_e(TCSCF+PT2) - D_e(TCSCF) \tag{15}$$

It follows, therefore, from eqs 14 and 15, and from the equivalence of TCSCF and VBSCF, that the resonance energy RE$_{CS}$ can be estimated at the level of dynamic correlation by simply adding the ΔDDE to the RE$_{CS}$ obtained at the TCSCF level:

$$\begin{aligned} RE_{CS}&(TCSCF+PT2) \\ &= RE_{CS}(TCSCF) + \Delta DDE(MO\text{-}based) \end{aligned} \tag{16}$$

Table 2 shows the impact of dynamic correlation on the dissociation energies and the RE$_{CS}$ quantities for the central bonds of H$_3$C−CH$_3$, NH$_2$−NH$_2$, HO−OH, and F−F, where the TCSCF+PT2 values are computed by the CASPT2 method with the two configurations. It is seen that these ΔDDE corrections for dynamic correlation are significant in all cases, ranging from 14 to 26 kcal mol$^{−1}$, and bringing the TCSCF+PT2 or BOVB levels (entries 4 and 5) much closer to experiment compared with the TCSCF or VBSCF values that are devoid of dynamic correlation (entries 1 and 2). The equivalence of the MO- and VB-derived values is apparent. Thus, the RE$_{CS}$ values calculated at the TCSCF+PT2 level (entry 7), are of the same order of magnitude as the BOVB values (entry 7), though somewhat larger.

The most informative quantity in Table 2 is %RE$_{CS}$, because this is the quantity that determines the classical covalent or charge-shift character of the bond. It can be seen from Table 2 (entries 9 and 10) and Figure 5 that the TCSCF+PT2 and BOVB values of %RE$_{CS}$ behave alike, just as was found at the static correlation level (Table 1). Thus, here too there is MO−
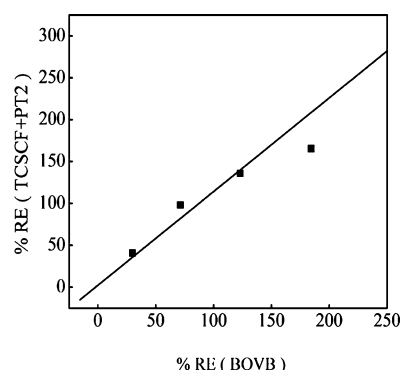
Figure 5. A plot of %RE$_{CS}$(TCSCF+PT2) vs %RE$_{CS}$(BOVB) for the bonds in Table 2

VB equivalence; the C−C bond is described as classically covalent, whereas N−N, O−O, and F−F bonds are CS bonds. As such, including dynamic correlation in the calculations basically yields more accurate values for dissociation energies and %RE$_{CS}$, and at the same time, it retains the bond types covalent vs CSB, as found already at the cruder VBSCF and TCSCF levels.

CONCLUSIONS

The charge-shift bonding concept was originally formulated in the VB framework and was later found to have clear signatures in density-oriented approaches like atoms-in-molecules (AIM) and electron-localization-function (ELF).[1,4−6,11,12] For example, unlike covalent bonds, such as C−C, for which the AIM derived Laplacian at the critical bond point is negative and indicative of stabilized shared density, in CSB like in F−F, the Laplacian is positive and typical of closed-shell repulsive interactions, indicating excess kinetic energy due to Pauli repulsion. Similarly, the bonding basin of covalent bonds has close to two electrons, as expected from a shared electron pair, whereas in a CSB bond like F−F, with its repulsive covalency, the bonding basin has 0.2 electrons or less. Moreover, CSB has signatures in experimental data.[1] For example, the experimentally determined positive Laplacian of the inverted C−C bond of [1.1.1] propellane as opposed to the negative value for the wing C−C bonds,[23] are in accord with the VB characterization of these bonds as CSB and covalent bond, respectively.[1] Importantly, as we showed, the RE$_{CS}$ property of CSB can be quantified from the difference in the experimental barriers of the H vs halogen (X) transfer reactions,[14] and more....[1] We now provide herein a proof of principle that an MO-based approach enables one to derive the charge-shift bonding (CSB) family as well as the distinctly different classical family of covalent bonds.

In this conceptual bridging approach, the covalent−ionic resonance energy (RE$_{CS}$) of a bond can be extracted from MO theory using an MO-based purely covalent reference state, which is defined as a constrained-two configuration (RTC) wave function. The energy gap between this latter state and the fully variational TCSCF ground state yields numerical values for RE$_{CS}$, which correlate with the values obtained at the VBSCF level. This simple MO-based method, which only takes care of static electron correlation, is already sufficient for distinguishing the classical covalent or polar-covalent bonds from charge-shift bonds.

The BOVB method dresses the VB structures with dynamic correlation and thereby provides more accurate values of RE$_{CS}$

and hence also better bonding energies. As we demonstrated above, an equivalent dynamic dressing energy correction can be obtained from an MO-based approach using TCSCF+PT2 calculations. As such, the application of dynamic energy correction improves the quality of the numbers, but does not change the physical picture of bonding and the emergence of a CSB family alongside the classical family of covalent bonds. It follows therefore, that the "existence" of the covalent and CSB families can be reasoned either from VB theory or from MO theory using the same reference state.

In fact, the RTC/TCSCF approach can be used to also drive the family of ionic bonds and to reveal the ionic−covalent crossing as expected for this bond type. A typical example of the Na$^+$F$^−$ bond is relegated to the Supporting Information. Another MO-based approach that enables calculating the energy gap between a fully ionic structure and a mixture of covalent and ionic structure is the well-established block-localized-wave function (BLW) method of Mo et al.[24]

What follows, therefore, from the above study is that the VB picture of three electron-pair bonding families (see Scheme 1) can be completely derived from an equivalent MO-based approach.[25] This provides further support for the existence of the CSB family as a distinct class alongside the classical covalent and ionic families. Recalling that the existence of the CSB family is associated also with quite a few experimental observations that we already reviewed (a few are mentioned above),[1,4,9,12−14,23] the new bonding concept has passed by now two stringent tests. This derivation, on the one hand, provides support for the CSB concept, and on the other, it creates conceptual bridges between the two main theories of chemical bonding.

METHODS

VB Method. In VB theory, a many-electron wave function is expressed as a linear combination of all of the VB structures that can be generated by distributing the electrons in the AOs/HAOs, as expressed in eq 17:

$$\Psi_{VB} = \sum_K C_K \Phi_K \tag{17}$$

where the Φ_K corresponds to a classical VB structure. The coefficients C_K are subsequently determined by solving the usual secular equation HC = EMC, where Hamiltonian and overlap matrix elements are defined as

$$H_{KL} = \langle \Phi_K | \hat{H} | \Phi_L \rangle \tag{18}$$

and

$$M_{KL} = \langle \Phi_K | \Phi_L \rangle \tag{19}$$

For a molecule of a single two-electron bond, the wave function is

$$\Psi_{VB} = C_1 \Phi_{cov} + C_2 \Phi_{ion} + C_3 \Phi'_{ion} \tag{20}$$

And weights of VB structures are determined by the Coulson−Chirgwin formula

$$W_{KL} = \sum_L C_K C_L M_{KL} = C_K{}^2 + \sum_{K \neq L} C_K C_L M_{KL} \tag{21}$$

In VBSCF,[26] both VB orbitals and structure coefficients are simultaneously optimized to minimize the total energy. In BOVB,[17] both orbitals and coefficients are optimized, with different orbitals for different VB structures. Both VBSCF and

H

dx.doi.org/10.1021/ct500367s | J. Chem. Theory Comput. XXXX, XXX, XXX−XXX

BOVB methods were used in their most accurate option of accuracy, respectively, D-VBSCF and SD-BOVB levels (see Supporting Information).

All VB and RTC calculations are performed by using XMVB,[27] which is an ab initio VB program, and TCSCF and TCSCF+PT2 calculations are carried out by the GAMESS package.[28]

ASSOCIATED CONTENT

Supporting Information

Method description, results of VBSCF, BOVB, and TCSCF calculations, and derivation of covalent−ionic crossing for NaF. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
*S. Shaik. E-mail: sason@yfaat.ch.huji.ac.il.
*P. C. Hiberty. E-mail: philippe.hiberty@u-psud.fr.
*W. Wu. E-mail: weiwu@xmu.edu.cn.

Author Contributions
The paper was written through contributions by all authors. All authors have given approval to the final version of the paper.

Notes
The authors declare no competing financial interest.

ABBREVIATIONS

BOVB, breathing orbital VB; CSB; charge-shift bonding; RTC, reference two-configuration; TCSCF, two-configurations self-consistent field; VBSCF, valence bond SCF

REFERENCES

(1) Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. *Nat. Chem.* **2009**, *1*, 443−449.
(2) Sini, G.; Maître, P.; Hiberty, P. C.; Shaik, S. S. *J. Mol. Struct.: THEOCHEM* **1991**, *229*, 163−188.
(3) Shaik, S. S.; Maître, P.; Sini, G.; Hiberty, P. C. *J. Am. Chem. Soc.* **1992**, *114*, 7861−7866.
(4) Shaik, S.; Danovich, D.; Silvi, B.; Lauvergnat, D.; Hiberty, P. C. *Chem.—Eur. J.* **2005**, *11*, 6358−6371.
(5) Jenkins, S.; Kirk, S. R.; Guevera-García, A.; Ayers, P. W.; Echegaray, E.; Torro-Labbe, A. *Chem. Phys. Lett.* **2011**, *510*, 18−20.
(6) Rzepa, H. S. *Nat. Chem.* **2010**, *2*, 390−393.
(7) Shaik, S.; Hiberty, P. C. *A Chemist's Guide to Valence Bond Theory*; Wiley-Interscience: New York, 2008.
(8) Braïda, B.; Hiberty, P. C. *Nat. Chem.* **2013**, *5*, 417−422.
(9) Hiberty, P. C.; Ramozzi, R.; Song, L.; Wu, W.; Shaik, S. *Faraday Discuss.* **2007**, *135*, 261−272.
(10) (a) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*. Oxford University Press: Oxford, U.K., 1990. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893−928.
(11) (a) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397−5403. (b) Savin, A.; Jepsen, O.; Flad, J.; Anderson, O. K.; Preuss, H.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 187−188. (c) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683−686.
(12) Wu, W.; Gu, J.; Song, J.; Shaik, S.; Hiberty, P. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1407−1410.
(13) Su, P.; Song, L.; Wu, W.; Shaik, S.; Hiberty, P. C. *J. Phys. Chem. A* **2008**, *112*, 2988−2997.

(14) Hiberty, P. C.; Megret, C.; Song, L.; Wu, W.; Shaik, S. *J. Am. Chem. Soc.* **2006**, *128*, 2836−2843.
(15) The simultaneous optimization of active constrained orbitals and inactive orbitals belonging to the same irreducible representation would make the covalent reference Ψ_{RTC} collapse to a solution close to the Ψ_{TCSCF} ground state.
(16) Ploshnik, E.; Danovich, D.; Hiberty, P. C.; Shaik, S. *J. Chem. Theory Comput.* **2011**, *7*, 955−968.
(17) (a) Hiberty, P. C.; Flament, J. P.; Noizet, E. *Chem. Phys. Lett.* **1992**, *189*, 259−265. (b) Hiberty, P. C.; Humbel, S.; Byrman, C. P.; van Lenthe, J. H. *J. Chem. Phys.* **1994**, *101*, 5969−5676. (c) Hiberty, P. C.; Shaik, S. *Theor. Chem. Acc.* **2002**, *108*, 255−272.
(18) (a) Wu, W.; Song, L.; Cao, Z.; Zhang, Q.; Shaik, S. *J. Phys. Chem. A* **2002**, *106*, 2721−2726. (b) Song, L.; Wu, W.; Zhang, Q.; Shaik, S. *J. Comput. Chem.* **2004**, *25*, 472−478.
(19) Chen, Z.; Song, J.; Shaik, S.; Hiberty, P. C.; Wu, W. *J. Phys. Chem. A* **2009**, *113*, 11560−11569.
(20) Wu, W.; Su, P.; Shaik, S.; Hiberty, P. C. *Chem. Rev.* **2011**, *111*, 7557−7593.
(21) For a beautiful illustration of the role of ionic structures, see: Goodgame, M. M.; Goddard, W. A., III *Phys. Rev. Lett.* **1985**, *54*, 661−664.
(22) Actually, because the electrons in the lone pairs are left uncorrelated statically, going from VBSCF to BOVB brings only the part of dynamic correlation that is associated with the formation of the bond.
(23) Messerschmidt, M.; Scheins, S.; Grubert, M.; Patzel, M.; Szeimies, G.; Paulmann, C.; Luger, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 3925−3928.
(24) (a) Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687−1697. (b) Mo, Y.; Zhang, Y.; Gao, J. *J. Am. Chem. Soc.* **1999**, *121*, 5737−5742. (c) Mo, Y.; Song, L.; Wu, W.; Zhang, Q. *J. Am. Chem. Soc.* **2004**, *126*, 3974−3982.
(25) For a MO perspective on CSB, see: Porrane, R. G.; Stanger, A. *ChemPhysChem* **2012**, *13*, 2377−2381.
(26) (a) van Lenthe, J. H.; Balint-Kurti, G. G. *Chem. Phys. Lett.* **1980**, *76*, 138−142. (b) van Lenthe, J. H.; Balint-Kurti, G. G. *J. Chem. Phys.* **1983**, *78*, 5699−5713. (c) Verbeek, J.; Verbeek, J.; Van Lenthe, J. H. *J. Mol. Struct.: THEOCHEM* **1991**, *229*, 115−137. (d) Van Lenthe, J. H.; Verbeek, J.; Pulay, P. *Mol. Phys.* **1991**, *73*, 1159−1170.
(27) (a) Song, L.; Chen, Z.; Ying, F.; Song, J.; Chen, X.; Su, P.; Mo, Y.; Zhang, Q.; Wu, W., *XMVB* 2.0: An ab Initio Non-orthogonal Valence Bond Program; Xiamen University: Xiamen, China, 2012. (b) Song, L.; Mo, Y.; Zhang, Q.; Wu, W. *J. Comput. Chem.* **2005**, 514−521. (c) Song, L.; Song, J.; Mo, Y.; Wu, W. *J. Comput. Chem.* **2009**, *30*, 399−406.
(28) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.*, **1993**, *14*, 1347−1363. See: http://www.msg.ameslab.gov/GAMESS/GAMESS.html.