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The Charge-Shift Bonding Concept. Electron-Pair Bonds with Very Large Ionic-Covalent Resonance Energies

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Abstract: The bonding mechanism in a variety of electron-pair bonds is studied by means of an ab initio valence bond method specifically designed for a rigorous separation of the covalent Heitler–London and the ionic contributions to the bond energy. While a number of bonds (H–H, H_3C–H, H_3Si–H, Li–Li, Na–F) are found to correspond to the traditional covalent (Heitler–London) or ionic pictures, some other bonds, even homopolar ones (H_2N–NH_2, HO–OH, F–F), have an unbound or weakly bound covalent component. These latter bonds do not owe their stability to the low energy of either the covalent or the ionic components, but rather to a very large resonance energy (53–79 kcal/mol) between these valence bond structures and as such are named "charge-shift bonds". Two general observations about electron-pair bonds are shown to be indirect marks of charge-shift bonding. These are Sanderson's "lone-pair bond weakening effect" and the finding of negative standard electron deformation densities in the bonding region. The stabilization brought by charge-shift bonding is shown to derive from the decrease of the electronic kinetic energy at the bonding region. Its magnitude correlates with the compactness of the valence orbitals involved in the bond and is reinforced by the presence of lone pairs adjacent to these orbitals. Larger and larger resonance energies are predicted as the bonded atoms change from left to right and from bottom to top of the Periodic Table. Other trends and features of charge-shift bonds are discussed.

I. Introduction

By tradition we consider electron-pair bonding in terms of two paradigms:[2] the "covalent bond" and the "ionic bond". These two bond types are associated generally with distinct physical and chemical behaviors which substantiate the classification on a firm practical basis.

From the viewpoint of quantum chemistry, the term "covalent" means that most of the bond energy originates in the spin-pairing itself, be the bond homopolar or heteropolar. In contrast, the term "ionic" means that most of the bond energy derives from the electrostatic stabilization of the oppositely charged ions with a marginal role assigned to the spin-pairing energy.

Recently, we have observed by computational means[3] that certain electron-pair bonds, *be they homopolar or heteropolar*, possess extremely large covalent–ionic resonance energies (defined as the stabilization of the optimal covalent–ionic mixing relative to the pure covalent or ionic forms). So large are these resonance energies that bonding itself owes its entire origin to the covalent–ionic resonance and cannot be associated with either the covalency or ionicity of these bonds. Certainly, at least in the homopolar bonds, any description of the bonding other than "covalent" is by definition puzzling and intriguing.

Even more appealing is the fact that this feature of bonding appears to coincide with two other observations on these bond types. Thus, the same bonds which are sustained by large resonance energies, e.g., F–F and C–F, etc., coincide with the bonds which are found to possess negative or only marginally positive deformation electron density in the bonding regions (also called sometimes no-density bonds).[4,5] A second observation is the "lone-pair bond weakening effect" (LPBWE) which was identified by Sanderson[2b] as an atomic property which the atom carries over to its bonds, and which typifies exactly those bonds that possess negative deformation densities and large ionic–covalent resonance energies.[3] It may well be then that the large ionic–covalent resonance energy which was found computationally is a fundamental bonding feature which possesses some characteristic physical and chemical signatures. Since we continue to discover this bonding feature in a variety of molecules, we feel that the problem merits further analysis and an attempt to understand the root causes of these large resonance energies and their possible consequences.

This paper presents multistructure valence bond (VB) computations[6,7] of bonding in a series of σ-bonds: H–H, Li–Li, H_3C–H, H_3Si–H, Na–F, F–F, H_3C–F, HO–OH, H_2N–NH_2, H–F, H_3C–F, and H_3Si–F. It will be shown that the bonds which possess large ionic–covalent resonance energies exist in a distinct class alongside the traditional bond types. The root causes of these large resonance energies will be analyzed and related to a fundamental bonding mechanism. As will be seen, the large ionic–covalent resonance energies, the LPBWE,[2b] and the negative deformation densities[5] of these bond types all have the same origins: the decrease of the kinetic energy of the bonding electrons in the internuclear region.[8]

II. Theoretical Methods

All calculations have been performed with a multistructure ab initio valence bond (VB) method which has been described in details in previous papers.[3,6] An essential feature of this method is that it deals with orbitals strictly localized on single bonding atoms or fragments with no delocalization tails. In this form, this is a "pure-VB" method which preserves faithfully the relationship between the VB functions and the

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(5) The deformation density $\Delta\rho$ is defined as the difference: $\Delta\rho = \rho$(molecule) − ρ(promolecule of nonbonded atoms). A negative $\Delta\rho$ in the internuclear region means depletion of electron density due to bonding, relative to the promolecule. There are a few definitions of the promolecule, and the standard deformation density refers to a promolecule of spherically averaged atoms. The reported negative $\Delta\rho$ values (ref 4 here) refer to the standard deformation densities. For discussions and analyses of $\Delta\rho$, see: (a) Low, A. A.; Hall, M. B. *J. Phys. Chem.* **1990**, *94*, 628. (b) Kunze, K. L.; Hall, M. B. *J. Am. Chem. Soc.* **1986**, *108*, 5122. (c) Schwarz, W. H.; Valtazanos, P.; Ruedenberg, K. *Theor. Chim. Acta* **1983**, *68*, 471.

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Table I. Energies[a] of Configurations, Resonance Energies (RE), and Bond Energies of Single Bonds, A–B

entry	A–B	$E_{HL}(A{\cdot}\!-\!{\cdot}B)$	$E_Z(A^+B^-)$	$E_Z(A^-B^+)$	RE	D(theor)	D(exptl)
1	H–H	−95.9	+37.3	+37.3	7.3	103.2	109.5[b]
2	Li–Li	−14.7	+1.5	+1.5	2.5	17.2	24.4[c]
3	H_3C-H	−89.7	+99.8	+18.7	11.1	100.8	110.3[d]
4	H_3Si-H	−81.8	−0.7	+76.3	6.8	88.6	95.3[d]
5	Na-F	+22.2	−101.9	+434.2	0.6	102.5	123.6[b]
6	F-F	+35.4	+251.3	+251.3	75.1	39.7	38.3[d]
7	HO-OH	+14.0	+202.2	+202.2	58.9	44.9	51.0 ± 1; 55.0[e]
8	H_2N-NH_2	−11.0	+147.9	+147.9	49.0	60.0	65.8[f]
9	H_3C-F	−28.3	+15.4	+488.7	70.9	99.2	112.7 ± 2[f]
10	H-F	−50.7	−43.4	+426.5	79.4	130.1	141.1[d]
11	H_3Si-F	−65.3	−92.2	+529.0	53.1	145.3	158.3 ± 6[g]

[a] In kcal/mol. All energies are relative to the sum of the fragment energies (A·+·B). [b] Reference 12a. [c] Reference 12b. [d] D_0 values are based on enthalpies of formation at 0 K, taken from ref 12c for CH_4, SiH_4, CH_3, F, and H. [e] Reference 12g,h. [f] Reference 12g. [g] References 12e and 12f.

chemical Lewis structures that are used to characterize the various types of bond (e.g., covalent and ionic).

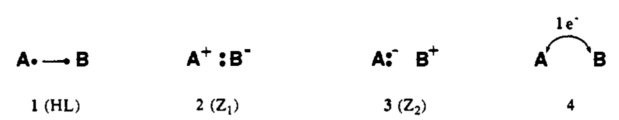
In this paper all the VB structures necessary for a quantitative description of a two-electron bond, i.e., one purely covalent and two ionic structures, are considered. Each one of them is described, in turn, by a linear combination of configuration state functions (CSFs) of VB type (previously referred to as VBFs[3]). The energy of a VB structure is computed accordingly by the variational mixing of an elementary CSF, built with Hartree–Fock-optimized fragment orbitals, with all the Brillouin states that can be generated from this elementary CSF by intrafragment monoexcitations, and that represent the same VB structure.

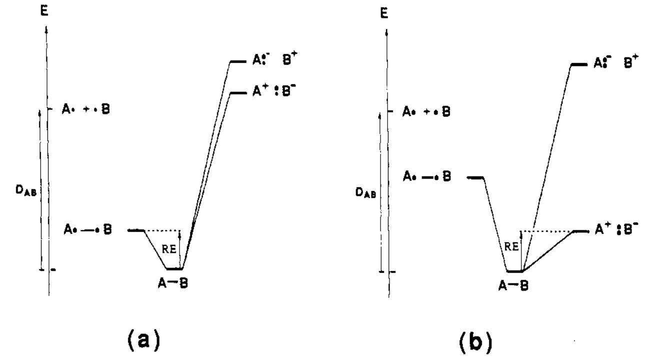
The bond energy is calculated by configuration interaction (CI) in the space of all the CSFs that are necessary for the description of each VB structure, covalent and ionic. In each case the same CI space has been generated for the molecule and the separated fragments to ensure consistency of the calculations. It has been shown in preceding papers[9] that the result of this CI is equivalent, to first order, to a nonorthogonal MCSCF calculation of a VB wave function reduced to its essential VB components (here one covalent and two ionic CSFs), in which the CSF coefficients and orbitals are optimized simultaneously. Each such CSF has *its own specific set of orbitals, optimized in the presence of the other CSF's, but different from one CSF to the other.* This last feature ensures the correct description of the ionic components and has been shown to be essential for quantitative estimates of some bond energies.[9]

The non-orthogonal CI among the valence bond CSF's has been performed with a program written by Lefour and Flament.[6e] The MONSTERGAUSS program[10] has been used for the initial Hartree–Fock optimizations of the fragment orbitals. The geometries and basis sets for most of the molecules are reported in ref 3. All basis sets are of double-zeta plus polarization quality, with the exception of Li_2 which was computed at the double-zeta quality. The bond energies for HO–OH and H_2N–NH_2 have been calculated with the 6-31G** basis set using experimental geometries.[11]

III. Results and Discussion. The Charge-Shift Bonding Concept

A. Results. Table I shows the results for a few σ-bonds of the general type A–B.[12] Considering the modesty of the basis sets





(a) (b)

Figure 1. A VB mixing diagram for structures **1–3** for (a) a case where the lowest structure is the HL configuration, and (b) a case where the lowest structure is ionic. RE is the charge-shift resonance energy.

used in the calculations, the calculated bond energies, D(theor), compare well with the experimental values, D(exptl). This satisfactory fit indicates the reliability of the VB method for probing the problem of bond energy on a quantitative basis.

The first three columns in Table I list the energies of the Heitler–London (HL) and ionic ($Z_{1,2}$) structures, which are depicted in **1–3** and which contribute to the makeup of the bond in the language of pure VB theory.[2a] The energies of the VB structures are reported in the table relative to the constituent radical fragments, A• and B•, at infinity. Thus, for example, when $E_{HL} > 0$, this means that the spin-paired HL structure, **1**, is less stable than its separated radical fragments, while when E_{HL} is negative, this means that the covalent spin-pairing is stabilized relative to the same fragments. The energy of the ionic structures is generally positive with two exceptions in entries 5 and 11, where the ionic structures are more stable than the respective two radical fragments. We emphasize that the bond energy due to spin-pairing, D_{HL}, is related to E_{HL} by simply inverting the sign, that is, $D_{HL} = -E_{HL}$.

The rest of the columns in the table can be understood in the light of the VB mixing diagram[13] in Figure 1 which shows the generation of the final electron-pair bond from the VB mixing of the structures. Using common perturbation theoretic approach,[14] the stabilization energy due to the mixing is measured relative to the energy of the lowest VB configuration. This quantity is the resonance energy stabilization due to the ionic–covalent mixing, and appears in the table under the column entitled "RE". Since all stabilization energies in VB theory can be couched in terms of resonance,[2a] we refer to this resonance energy hereafter as the *charge-shift resonance*. This term describes the particular mode of resonance between two structures which can be generated from each other by a shift of a single electron between the con-

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stituent fragments of the bond as shown pictorially in **4**.

Inspection of the RE quantity in Table I reveals three types of bonding. In entries 1–4 the major bonding arises from the spin-pairing in the HL structure, while the charge-shift resonance contributes a small fraction of the bonding energy (3–11 kcal/mol). These bonds owe their existence to the spin-pairing stabilization and follow thereby the traditional sense of covalent bonding. In entry 5 we encounter a traditional ionic bond, NaF, for which most of the bonding energy (>99%) is provided by the ionic structure $Na^+{:}F^-$.

In the above two traditional types, the principal configurations themselves (either HL or Z_1) are responsible for most of the bonding energy, while the RE is a minor bonding event. In contrast, entries 6–11 exhibit a completely different behavior. Thus, in all the cases, in entries 6–10, the lowest VB structure is the HL covalent configuration, but it brings either meager bonding or not at all. In comparison with the inefficient HL bonding in these bonds, the corresponding RE quantities are very large. In fact, the F–F and O–O bonds in entries 6 and 7 owe their raison d'etre to the charge shift resonance, *while their HL structures are repulsive*. Similarly, in entry 11 the lowest VB structure is the ionic $H_3Si^+{:}F^-$ structure, yet the bond possesses a very large RE of 53.1 kcal/mol. In all these cases, therefore, unlike the traditional types, the nature and *stability of the major VB structure is a secondary factor while the RE constitutes now the major bonding event*.

An important point to ensure, at this point, is that our findings are not merely the results of a computational artifact, and that the charge-shift terms are not given an arbitrary importance. In that respect, it is well known that the coefficients of the ionic structures **2** and **3** depend on the type of VB method that one uses. Dealing with orthogonalized AOs, for example, is known to lead to very large ionic coefficients. Alternatively, it is also possible to describe the electron-pair bond as a formally covalent wave function, built with AO-like orbitals in the sense that they are centered mostly on one fragment, but have a non-negligible tail on the other fragment.[15] Thus the ionic and covalent weights depend on the choice of the orbitals that are used in the VB structures; the reason for this dependence originates in the various delocalization tails that these orbitals may bear. Indeed, when a delocalized "AO-like" orbital is occupied, it is not clear whether the electron should be considered as located on one fragment or the other, and therefore the distinction between ionic and covalent structures is not clear-cut, thus leading to a variety of VB structural weights depending on the nature of the orbitals. It is precisely in order to avoid this ambiguity, and to make sure that our ionic VB structures truly reflect a chemical charge separation between the two fragments, that we chose to define our VB structures with strictly local fragment orbitals bearing no delocalization tails of any kind on the other bonding fragment.

As for the physical nature of charge-shift in the two-electron bond, two points are noteworthy: (i) even the formally covalent descriptions of the electron-pair bonds implicitly involve some hidden ionic components, through the delocalization tails of the orbitals,[16] which allow the two electrons to be part of the time on the same fragment despite the formal single occupancy of the spin-coupled orbitals; and (ii) the physical essence of charge-shift terms has recently been demonstrated on the F_2 molecule.[9b] Indeed, the explicit inclusion of structures **1–3** in a three-configuration VB function using strictly local AOs leads to a bond energy in excellent agreement with the full CI result, while the purely covalent wave function with optimally delocalized orbitals, with the same basis sets, accounts only for nearly half the correct bond energy. It follows therefore that the mixed covalent–ionic description is an essential feature of bonding, and that both the covalent and ionic structures must be treated explicitly and on equal footing.

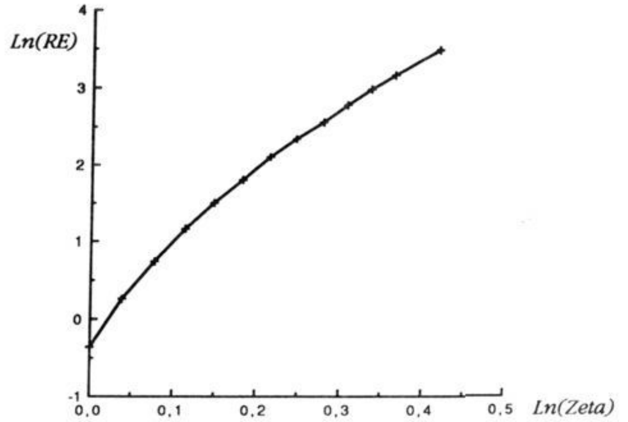


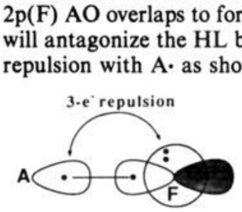
Figure 2. A log–log plot of RE versus orbital exponent η for a pseudo-H_2 molecule. The calculations are performed with a minimal basis set.

Having reasoned that the large charge-shift resonance effect is not simply a mathematical curiousity of the nonorthogonal VB method, we feel quite confident to define the unique bonding feature in entries 6–11 of Table I as *charge-shift bonding*. Let us turn now to discuss the trends which characterize this bonding type, specifically, the weakened HL bond and the large RE.

B. Destabilization of the HL Configuration and Sanderson's LPBWE. In Table I, the charge-shift bonds are restricted to the electronegative atoms, F, O, and N. Furthermore all of these bonds are typified by a HL configuration which is either marginally bound or unbound ($D_{HL} < 0$). In the case of the F atom, we have a few heteropolar A–F bonds, and in all of them it is seen that F carries over its HL bond weakening effect to all of its bonds. In the previous publication[3] this was demonstrated by the simple fact that the HL bond energy obeys approximately the averaging procedure:

$$D_{HL}(A\cdot\!\!-\!\!\cdot B) = [D_{HL}(A\cdot\!\!-\!\!\cdot A) + D_{HL}(B\cdot\!\!-\!\!\cdot B)]/2 \quad (1)$$

It follows from eq 1 that, when a certain fragment possesses a weakened homonuclear HL bond, the effect carries over to the heteronuclear HL bond. This HL bond weakening is then an inherent property of the atom or fragment as deduced by Sanderson.[2b] This property has been discussed previously[3] and will be repeated in brevity here, by appeal to the archetypal case of A–F bonds. Fluorine possesses 2p and 2s AO's which can overlap with the bond orbital of fragment A. While the singly occupied 2p(F) AO overlaps to form the HL A·–·F bond, the filled 2s AO will antagonize the HL bond by virtue of three-electron overlap repulsion with A· as shown schematically in **5**.



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The energy expressions of the HL bonding and the three-electron overlap repulsion are approximately equal but possess opposite signs, that is, $\pm 2\beta S$.[13] Since the overlap capability of 2s(F) is larger than that of 2p(F),[17,18] the overlap repulsion is acute and larger than the HL bonding. Of course, if the second fragment A possesses also a filled orbital of the same symmetry as the bond hybrid and with a good bonding capability, the resulting overlap repulsion will be extremely large and the HL structure highly repulsive. If F was free to hybridize its 2s–2p AOs, at no cost, this would have simply reduced the overlap repulsion and improved

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the HL bonding as sketched in **6**. However, the hybridization is equivalent to a fractional 2s → 2p excitation (promotion), and, since the promotion energy is very large (542 kcal/mol[3]), the hybridization has to occur against a very large cost and does not effectively reduce the overlap repulsion, **5**. This is the reason why the HL bond energies for A–F bonds are weak, and in the F–F case the HL bond is even unbound.

These arguments are generally valid for the first-row electronegative atoms, F, O, and N, which possess 2s AOs which overlap as well or even better than the singly occupied 2p AO which should be responsible for the HL spin-pairing with a partner fragment. However, as the atom increases in size along the series, the overlap repulsion decreases because the 2s orbital has a higher energy,[19] and at the same time the cost of hybridization decreases and the hybridization reduces the repulsion more effectively. Consequently, as seen in Table I, the HL bond weakening effect becomes less pronounced as we progress from F–F through O–O to N–N. In the same vein of thought, we expect a heteronuclear HL bond weakening to follow the order $D_{\mathrm{HL}}(\mathrm{A}{\cdot}{-}{\cdot}\mathrm{F}) < D_{\mathrm{HL}}(\mathrm{A}{\cdot}{-}{\cdot}\mathrm{O}) < D_{\mathrm{HL}}(\mathrm{A}{\cdot}{-}{\cdot}\mathrm{N})$. In conclusion, the LPBWE which was discussed by Sanderson[2b] is associated with the weakening of the spin-pairing bonding by overlap repulsion of filled AOs which possess the same symmetry as the HL bond itself. As a general trend, the HL bond weakening and its associated LPBWE are expected to increase as the atoms vary from left to right and from bottom to top in the Periodic Table.

C. Charge Shift Resonance Energy. Its Trends and Origins. Despite its magnitude, the LPBWE does not preclude the formation of bonds, and this is because weak or repulsive HL bonds coincide with large RE's. This fact suggests a connection between LPBWE and charge-shift bonding. More generally, inspection of the computational results for the homopolar or quasi-homopolar bonds in the series Li–Li, CH_3–H, H_2N–NH_2, HO–OH, and F–F reveals that the charge-shift resonance RE increases as the constituent atoms change from left to right in the Periodic Table. What is the origin of this tendency?

Intrinsic Two-Electron Effect: The Compactness of the Bonding Orbitals. An intuitive reasoning may help us to understand the physical meaning of the charge-shift resonance between covalent and ionic structures in a bond. Let us use an example where the covalent HL structure is the lowest one. By simply blending in the ionic structures the electronic system will merely raise its potential energy, since the ionic structures possess higher potential energy. Nevertheless, the actual mixing is stabilizing, and the reason can only lie in a lowering of the kinetic energy in the bonding region.

We may also understand this stabilization as a consequence of the allowance of the bonding electrons to approach each other for dynamical reasons, rather than being confined in the limitations of a purely covalent structure. This confinement is expected to be more severe as the orbitals get more compact with a larger orbital exponent, thus leading to an increased role of the ionic structures and to larger RE's. If this is true, then starting from the H_2 wave function at equilibrium distance with optimized exponents for the atomic orbitals, one should observe an increase of the RE as the AOs shrink by increasing their exponents. This is what we observe, in fact, in Figure 2, which shows the resulting RE values against the orbital exponent of a H_2 molecule made of pseudo-H atoms with variable orbital exponents in the 1s AOs.

The problem may be tackled also in a mathematical way, by expressing the RE as in eq 2 in terms of the reduced resonance

$$\mathrm{RE} \sim |\beta^2/[E_{\mathrm{HL}} - E_{\mathrm{Z_{opt}}}]| \qquad (2)$$

integral β and the configuration energy gap between HL and $\mathrm{Z_{opt}}$, where $\mathrm{Z_{opt}}$ is the optimized linear combination of structures **2** and **3**. We note that this β integral and those β's which appear in the HL bonding and overlap repulsion expressions are of the same identity, and we may therefore carry over arguments from one type of reduced resonance integral to the other.[13] It is with this qualification that we follow Kutzelnigg's[8] treatment which shows that β is generally made of a dominant negative kinetic component, β_{T}, and a smaller and positive potential component, β_{V}. It follows, therefore, that the charge-shift resonance energy, which results from the mixing of ionic structures into the HL structure, acts mainly to lower the kinetic energy in the bonding region. Thus, the large RE which typifies charge-shift bonding is associated with the lowering of the kinetic energy in the bonding region.[20]

Kutzelnigg[8] has also given an approximate expression for β_{T} as a function of η, the orbital exponent, and the internuclear distance R:

$$\beta_{\mathrm{T}} = -1/3[\eta^4 R^2 e^{-\eta R}] \qquad (3)$$

If indeed the kinetic energy term β_{T} dominates the charge-shift resonance energy, RE, in eq 2, then this latter quantity should be a very sensitive function of the orbital exponent. In such a situation, eqs 3 and 2 together show that RE should increase approximately as the eighth power of η. This prediction is well substantiated in Figure 2, where the slope of the log–log plot of RE versus η is 8.89, thus showing indeed quite a great sensitivity of the charge shift resonance energy to the compactness of the orbital.

We can further understand the above results of our computational experiment by considering the virial relation for a stationary point (5) between the kinetic (T) and potential (V) components of the total energy E (4) of the molecule:

$$E = T + V \qquad (4)$$

$$T = -\tfrac{1}{2}V \qquad (5)$$

Let us start from an optimal wave function which obeys the virial theorem, eq 5, for H_2 with optimal η for the experimental geometry, and gradually shrink the orbital (larger η). This will raise the kinetic energy and lower the potential energy of the electrons, and, since we start from an equilibrium situation, these changes will be equal but with opposite signs, as follows:

$$\partial V/\mathrm{d}\eta = -\partial T/\mathrm{d}\eta \quad (\partial T > 0) \qquad (6)$$

The result is that the virial theorem is now disobeyed since:

$$T + \partial T > -\tfrac{1}{2}(V + \partial V) \qquad (7)$$

Even if the theorem does not have to be obeyed in such an away-of-equilibrium situation, we can nevertheless expect a driving force to restore the virial relationship by lowering the kinetic energy through an increase of the covalent–ionic mixing. This as we discussed above lowers the kinetic energy by increasing the contribution of the charge-shift resonance to the bonding. The inverse result is evidently expected when η decreases and the orbital becomes more diffuse. In conclusion, large charge-shift resonance energies are expected to be characteristic of compact orbitals. Indeed as can be seen in Table I, the magnitudes of the RE quantity nicely follow the orbital compactness in the series Li–Li, H–H, C–H, N–N, O–O, and F–F.

Effect of the Neighboring Lone Pairs: Relation to the LPBWE. Similar considerations as above may be used to link large resonance energies to the LPBWE which is discussed in Section B. We recall that the LPBWE is due to three- and four-electron overlap repulsions between the lone pairs and the bond electrons

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(19) β is generally proportional to the energies of the orbitals which participate in the resonance integral. Both β and the orbital energies are negative quantities.

(20) Another reasoning, based on the GVB concept of the two-electron bond, may also explain how the admixture of ionic terms to the covalent component of a bond lowers the kinetic energy. As has been noted by Kutzelnigg,[8] the kinetic energy is related to the gradient of the wave function in the bond region: the flatter the wave function, the lower the kinetic energy. Now adding some ionic contributions to a covalent bond, in classical VB theory, is equivalent in GVB theory to a distortion of the bonding orbitals forming the GVB pair. In this distortion, each AO, formerly localized on a single fragment, is slightly delocalized on the other bonding fragment, and therefore the wave functions becomes flatter, thus leading to a lowering of the kinetic energy in the bonding region. See: Goddard, W. A.; Wilson, C. W. *Theor. Chim. Acta* **1972**, *26*, 211.

and between the adjacent lone pairs themselves. These overlap repulsive terms, which attend the formation of the bond, vary according to approximate VB theory[13] in proportion to $\sim\beta$ as discussed above by reference to **5**. Since β itself is negative, the main effect of these repulsive terms is *to raise the kinetic energy*,[8] which in turn has to be compensated by a kinetic energy decrease to restore the virial relation (eq 5). The mechanism for the lowering of the kinetic energy is the increased extent of the ionic–covalent mixing which increases the RE contribution to the bonding. As the atomic orbitals become more compact, all the reduced resonance integrals become larger in absolute magnitude,[19] and as a result the smaller is the constituent atom the larger the overlap repulsion associated with the lone-pair bond weakening effect and the more important is the charge-shift resonance in bonding.

It appears, therefore, that the large charge-shift resonance energies that are observed in the bonds involving the N, O, and F atoms are due to a combination of the orbital compactness of these atoms and the lone-pair–bond-pair repulsions associated with the LPBWE. While the latter effect overrides the covalent HL bonding, the former effect provides the main source for the bonding of the two fragments or atoms via the charge-shift mixing. In VB terms this is expressed by trading off the spin-pairing covalent bonding for charge-shift bonding. We may conclude therefore that, as we move from left to right and from bottom to top in the Periodic Table, the valence orbitals contract and there will be an increased propensity of the atom to form homopolar and heteropolar charge-shift bonds.

D. Relationship between Negative Deformation Densities and Charge-Shift Bonding. As mentioned in the Introduction, the same bonds that are characterized by LPBWE and charge-shift character, e.g., F–F, O–O, etc, are also found to exhibit negative standard deformation densities, $\Delta\rho$(std). On the other hand, covalent bonds like H_2, Li_2, C–C, C–H, etc., are found to possess positive $\Delta\rho$(std).[4,5] The mechanisms for the negative $\Delta\rho$(std) quantity have been discussed lucidly by Hall and collaborators[5a,b] and by Ruedenberg and collaborators[5c] in terms of electron density reorganization. Our own aim here is simply to elucidate the connection of the negative $\Delta\rho$(std) to charge-shift bonding.

Using a standard definition of a promolecule, made of spherically averaged atoms,[5] a covalent bond like H–H is associated with a positive $\Delta\rho$(std) which indicates that upon spin-pairing in the HL structure and bond formation there is a buildup of electron density at the internuclear region. In contrast, the negative or marginally positive $\Delta\rho$(std) for charge-shift bonds arises as a result of the overlap repulsion between the lone pair and the bond pair, in the HL covalent structure, **5**, and is indicative therefore of the unimportance of the HL bonding. As a consequence of these repulsions, in the HL structure, the electrons avoid the antibonding interaction by polarizing away from the mid-bond to the outer-bond regions. Thus, the negative $\Delta\rho$(std) reflects the kinetic energy rise at the bonding region due to the HL bond weakening and its associated LPBWE. As discussed above, this kinetic energy rise is compensated in part by an increased importance of charge-shift bonding which lowers the kinetic energy at the bonding region. It follows, thereby, that large charge-shift resonance energies should correspond in general to a negative standard deformation density, and that this latter phenomenon is an indirect mark of charge-shift bonding.

E. Is Charge-Shift Bonding Always Associated with the LPBWE and with Negative Standard Deformation Densities? The root of the link that appears to exist between charge-shift bonding, on the one hand, and the LPBWE and negative $\Delta\rho$(std), on the other hand, is the fact that those atoms which possess very compact valence orbitals are the same atoms which possess also lone pairs which antagonize the HL bonding. With this coincidence, the reduced resonance integrals dominate the trend and impart simultaneously high overlap repulsion and large charge-shift resonance. While this is certainly the case for most of the bonds in Table I, we must not ignore the second factor in eq 2, the configuration energy gap. Thus, cases may exist where the HL and ionic type configurations are degenerate or almost so. In such cases even modest reduced resonance integrals will impart large RE and establish charge-shift bonding, even if the constituent atoms do not have themselves a strong propensity to form homopolar charge-shift bonds. A particular case like that is the CH_3–NH_3^+ bond in which the HL configuration and the charge-shifted structure, CH_3^+:NH_3, are nearly degenerate and cause the bond to be stronger than its unprotonated analogue. This case has been discussed recently,[21] and we expect to find more cases of a similar nature, especially in heteropolar bonds of heavy elements.[21a]

IV. Concluding Remarks

This paper analyzes charge-shift bonding in electron-pair bonds. This bonding feature, which appears here in the bonds of F, O, and N, is found to exist as a distinct class alongside the traditional covalent and ionic bonds.[2,3] Bonding in charge-shift bonds is dominated by large resonance energies (53–79 kcal/mol) due to the mixing of the spin-paired Heitler–London (HL) structure ($A{\cdot}\!-\!{\cdot}B$) with the ionic structures ($A^{+}{:}B^{-}$ and $A{:}^{-}B^{+}$). Of course, the unique character of charge-shift bonds does not lie in the phenomenon of resonance itself, which has been known for decades,[2] but rather in the fact that the resonance energy can be overwhelmingly large, to such an extent that the ionicity and covalency become a feature of minor significance relative to the resonance energy. For example, the F–F, O–O, and N–N series of bonds is a unique series of homopolar bonds which by common wisdom will not be considered as anything else but covalent bonds. However, our results project the special status of these homopolar bonds and show that the origin of their bonding is the charge-shift resonance, while the covalent spin-pairing by itself ranges from very weakly stabilizing (N–N) to strongly destabilizing (F–F).

The Si–F bond constitutes another interesting case. Here the ionic structure $Si^{+}F^{-}$ is quite low in energy, lying 92.2 kcal/mol below the separated radical fragments and 27 kcal/mol below the covalent HL structure. However, the Si–F bond is by no means ionic in the traditional sense because it enjoys a very large charge-shift resonance energy of 53.1 kcal/mol. This is an important feature of many heteropolar charge-shift bonds: that despite their high charge separation, which implies "high ionicity", the bond *is not ionic* and will not behave so in the practical chemical sense. This is in accord with experimental findings that, for example, the seemingly ionic Si–F bond does not heterolize in solution, and that Ph_3Si–$OClO_3$ appears perfectly covalent-like in the solid state.[22]

To be a charge-shift binder the atom needs to possess compact valence orbitals and lone pairs which antagonize the spin-pair bonding in the HL structure by means of overlap repulsion. These two factors are manifested, in turn, as large charge-shift resonance energies. It is shown that in charge-shift binders the mechanism of lowering the kinetic energy at the bonding region is by means of trading the HL spin-pair bonding for the dynamic effect inherent in the charge-shift resonance. Using the orbital compactness as our organizing quantity, we are able to predict that the propensity for charge-shift bonding is expected to increase as the atom varies from left to right and from bottom to top at the Periodic Table. The exceptions to this rule are expected whenever the HL and its charge shifted structures become degenerate or nearly so.[21]

The relationship between charge-shift bonding, on the one hand, and, on the other hand, Sanderson's[2b] lone-pair bond weakening effect (LPBWE) and the negative standard deformation densities[4,5] of the same bonds is discussed. It is argued that these latter two observations are indirect marks of the existence of charge-shift bonding.

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Charge-shift bonding is essentially a new bonding paradigm, albeit with traditional roots, and as such it will be tested by the range of its applicability in chemistry. From preliminary observations[21,23] this bonding feature may turn out to be ubiquitous in bonding of heteropolar bonds, hypercoordinated molecules, and excited states. A task therefore lies ahead to find the chemical consequences of this bonding type on structure and reactivity.

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(23) Our preliminary VB computations for the hypercoordinated $(XMX)^-$ species show large RE values (65–93 kcal/mol) for the cases where X = F and M = CH_3, SiH_3, and H respectively, and small RE values for X = H.

Microscopic Modeling of Ligand Diffusion through the Protein Leghemoglobin: Computer Simulations and Experiments

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Abstract: The diffusion of carbon monoxide through lupine leghemoglobin was investigated. The potential of mean force, the transition-state theory rate constant, the friction kernel, the transmission coefficient, and the diffusion constant were calculated. The computations are based on our previous exploration of the diffusion dynamics using the mean field method (LES)[12] and on our calculation of the reaction coordinate.[13] The back of the heme pocket (close to phenylalanine 44 and phenylalanine 29) is a shallow free energy minimum for the dissociated ligand. The minimum is directly accessible (without a barrier) from the binding site. The barrier for escaping from the free energy minimum to the CE loop is low (approximately 3 kcal/mol). Once the ligand leaves the pocket, the diffusion is barrierless. The ligand escapes in two steps. In the first (activated) step the ligand is hopping from the heme pocket to the protein interior, and in the second step it diffuses through the protein matrix to the surface of the macromolecule. The transition-state theory (which is appropriate for activated processes) is used for the first part of the process. For the second part a diffusion model is constructed. The calculated friction kernel and its power spectrum strongly depend on the reaction coordinate. The power spectrum is consistent with previous interpretations of the diffusion dynamics. In the first step of the process the barrier is local and the power spectrum shows only high-frequency modes. In the second step significant coupling to low-frequency (extended) modes is observed, and the diffusion coordinate is dominated by motions of the C and the G helices of the protein. Experimental results for ligand rebinding kinetics in lupine leghemoglobin are reported. It is shown that different diatomic ligands have an unusually fast diffusion rate in accord with theory.

I. Introduction

The activated diffusion of a small ligand through a protein matrix attracted considerable attention in the past. Perutz[1] noted that, according to the X-ray structure of hemoglobin, there is no obvious way for the ligand to escape from the protein matrix to the solvent. Since then, thermal fluctuations of the protein, which open transient gates for the ligand diffusion, were the focus of a number of theoretical investigations.[2-12] There are two extreme atomic models of ligand diffusion which one may have in mind. One is of ligand escape along a well-defined and (almost) unique path, and the second is of diffusion through a large number of alternative channels. We call the first the "hole" model and the second the "sponge" model.

The pioneering calculations of Case and Karplus,[2] Case and McCammon,[7] and Kottalam and Case[8] focused on the application of the "hole" model to the protein myoglobin. Tilton et al. addressed the question of alternate paths by simulating the motion of a probe particle through a rigid[9] and flexible[10] myoglobin. Their studies suggest that the single path assumption may be too restrictive. Elber and Karplus[11] provided more support to the existencee of multiple paths in myoglobin. They employed their LES method to investigate the diffusion of carbon monoxide through myoglobin. The LES method was designed to provide efficient search for possible openings in a fluctuating protein structure; therefore, more paths were detected than in previous studies.[2,9,10] The searches were, however, approximate, and the existence of alternative diffusion routes still awaits experimental and theoretical verification.

It is of interest to extend the investigations of diffusion routes to other proteins, especially ones with significantly different binding properties. We investigated recently lupine leghemoglobin which is a "relative" of the protein myoglobin.[12,13] Leghemoglobins are plant proteins with a global fold similar to that of myoglobin. The binding properties of the two protein families are, however, very different. For example, in soybean leghemoglobin the diffusion rate is much faster than in sperm whale myoglobin.[14,15] Only

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