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A Simple Definition of Ionic Bond Order

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Abstract: Taking the square of the bond ionicity, $i_{\mu}^2(i,j)$, for molecular orbital μ in the localized orbital representation of Cioslowski and Mixon (*J. Am. Chem. Soc.* **1991**, *113*, 4142–4145) as an ionic bond order, one finds a simple and natural relation between the covalent bond order, $p_{\text{cov},\mu}(i,j)$, and the ionic bond order, $p_{\text{ion},\mu}(i,j)$: $p_{\text{ion},\mu}(i,j) \equiv i_{\mu}^2(i,j) = 1 - [p_{\text{cov},\mu}(i,j)]/[p_{\text{cov},\mu}^{\text{max}}(i,j)]$ where $p_{\text{cov},\mu}^{\text{max}}(i,j) = t_{\mu}(i,j)^2$ is the maximum value $p_{\text{cov},\mu}(i,j)$ can attain and where $t_{\mu}(i,j)$ is the total orbital occupancy of the atoms-in-molecules basins involved. A number of examples and limitations of the method are presented using the B3LYP/6–311+G(d,p) density functional approach.

I. Introduction

When chemists speak of chemical bonds they usually refer to them as “covalent” or “ionic” or, more generally, “polar” or “nonpolar”. When electron pairs are nearly equally shared between two atoms of similar electronegativities, we think of the bond holding the atoms together as a covalent or nonpolar bond. Likewise, when the electronegativity difference is large, such as in NaF, the electron pair is basically held much more by the more electronegative element, and we call the bond ionic or polar. But, of course, pure covalent bonds are rare, and there are in actuality no pure ionic bonds because the electron pair involved will have some spatial component of the less electronegative element (unless the bond is completely broken into ion fragments, in which case there is no bond at all!). More generally, bonds are polar, and the extent of their polarity dictates our qualitative way of discussing them. That is, all bonds have some covalent character, and virtually all bonds between elements of differing electronegativity have some ionic character.

While the general nature of the chemical bond has an implicit understanding among chemists, its quantitative character must be *defined* in terms of reasonable molecular quantities, and there are a multitude of such definitions. Covalent bond orders have been defined in a variety of ways and are useful quantities in that they tend to reflect in a quantitative way the covalent bonding involved. Not only can individual covalent bond orders be defined but

also total covalent bond orders for a given atom such as the atomic covalency of Ángyán, Loos, and Mayer.¹ The covalent bond order of Ángyán et al. and the equivalent single determinant form of the delocalization index of Fradera, Austen, and Bader² along with the covalent bond order of Cioslowski and Mixon³ (CM) can be used to measure such quantities. These bond orders have a strong theoretical foundation since they are based on the (spinless) electron pair density, most appropriate in discussing electron pairs. All these approaches employ the atoms-in-molecules (AIM) approach of Bader⁴ in which the electronic space is divided into disjoint basins based on the vector field of the gradient of the electron density, $\rho(\vec{r})$. We focus here on the approach of Cioslowski and Mixon defined in a basis of localized orbitals that allow the bond character to be more easily visualized.

But while covalent bond orders are readily defined, there has, to this point, been no corresponding simple and readily available definition of ionic bond order. In a recent paper Gould et al.⁵ suggest a definition for covalent and ionic bond indices that appears most promising, although it is not of immediate transparency. They point out that at the time of their publication the concept of an ionic bond index had not been thoroughly defined on an equal footing with the covalent bond index, and, in contrast to the present method (*vide infra*), their approach is not limited in its application. The purpose of our paper is to point out that such a bond order can be simply defined that readily follows the basic ideas of bond polarity. The defined ionic bond order is very natural, and its attractiveness lies in the ease with which it

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fits in and complements the corresponding Cioslowski-Mixon covalent bond order.

II. Theoretical Background

The covalent bond orders of Cioslowski and Mixon³ are directly related to and more transparently understood by the ideas of the covalent bond order of Ángyán, Loos, and Mayer¹ and the delocalization index of Fradera, Austen, and Bader.² The bond orders between AIM atoms (basins) i and j are defined by a decomposition of the spinless pair density, $P_2(\vec{r}_1, \vec{r}_2)$, a decomposition that is due to McWeeny^{6,7} who defined $P_2(\vec{r}_1, \vec{r}_2)$ in a way that accentuates the role of correlation by introducing the *correlation factor* $f(\vec{r}_1, \vec{r}_2)$.

$$P_2(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2)[1 + f(\vec{r}_1, \vec{r}_2)] \quad (1)$$

In terms of this expression for $P_2(\vec{r}_1, \vec{r}_2)$ one then finds the interbasin pair number, N_{ij} , to be given by

$$N_{ij} = \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 P_2(\vec{r}_1, \vec{r}_2) = \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 \rho(\vec{r}_1)\rho(\vec{r}_2)[1 + f(\vec{r}_1, \vec{r}_2)] = N_i N_j + \int_{\Omega_i} d\vec{r}_1 \int_{\Omega_j} d\vec{r}_2 \rho(\vec{r}_1)\rho(\vec{r}_2)f(\vec{r}_1, \vec{r}_2) = N_i N_j - F_{ij}(2)$$

which defines F_{ij} and holds for all i, j , including the case $i=j$. N_i is the (average) electron population of basin i . Fradera, Austen, and Bader³ define $F_{ii} \equiv \lambda_i$ as the *atomic localization index*, and the sum $F_{ij} + F_{ji} = 2F_{ij} \equiv \delta_{ij}$ as the *delocalization index*. They do not take the delocalization index as a bond order per se but rather as a measure of the number of electron pairs shared between basins i and j .

The nature of the delocalization index is more clearly seen when we express it for a closed shell, single determinant wave function (such as a Hartree–Fock wave function or the Kohn–Sham wave function employed here) where it is given by integration of the exchange density over the two basins involved

$$\delta_{ij} = 2F_{ij} = 4 \sum_{\mu, \nu}^{occ} \langle \mu | \nu \rangle \langle \nu | \mu \rangle_j \quad (3)$$

where standard bracket notation is employed, and where the subscripts i, j refer to basins Ω_i, Ω_j . Clearly the delocalization index is nonzero only if (molecular) orbitals span (extend into) both basins i and j . It will tend to more readily reflect a “true” bond order when polarization effects are absent but will be more complicated when such effects are present. In the single determinant approach the delocalization index given in eq 3 is *exactly* the topological covalent bond order defined by Ángyán, Loos, and Mayer.¹

The Cioslowski-Mixon (CM) bond order³ is found from a decomposition of the total number of electrons in the system. Employing the Bader-Stephens sum rule⁸ one can show that

$$N = \sum_{ij} F_{ij} = \sum_{ij} \sum_{\nu, \mu} 2 \langle \nu | \mu \rangle_i \langle \mu | \nu \rangle_j = \sum_{ij} \sum_{\mu} 2 \langle \mu | \mu \rangle_i \langle \mu | \mu \rangle_j + \sum_{ij} \sum_{\nu < \mu} 4 \langle \nu | \mu \rangle_i \langle \mu | \nu \rangle_j \quad (4)$$

However, the last term in the final expression in eq 4 vanishes due to orbital orthogonality, so that we finally obtain

$$N = \sum_{ij} \sum_{\mu} 2 \langle \mu | \mu \rangle_i \langle \mu | \mu \rangle_j = \sum_i \sum_{\mu} 2 \langle \mu | \mu \rangle_i \langle \mu | \mu \rangle_i + \sum_{i < j} \sum_{\mu} 4 \langle \mu | \mu \rangle_i \langle \mu | \mu \rangle_j \quad (5)$$

The expression for N in eq 5 is quite general for single determinant wave functions.

Cioslowski and Mixon start with the expressions in eq 5, defining the first ($i=j$) term as N_{atomic} and the second ($i < j$) as $N_{diatomic}$. They then perform an orbital localization procedure which maximizes N_{atomic} while maintaining the first order density matrix constant, Cioslowski’s *isopycnic* transformation,^{9,10} a generalization of the unitary transformation to which it reduces for single determinant wave functions where occupation numbers are unity or zero. Cioslowski and Mixon then *define* a covalent bond order, $p_{cov}(i, j)$, between AIM basins i and j in this specific representation as

$$p_{cov}(i, j) = \sum_{\mu} 4 \langle \mu | \mu \rangle_i \langle \mu | \mu \rangle_j \quad (6)$$

These bond orders generally relate well to conventional ideas of single and multiple covalent bonds, as do those in the more general and invariant approach used by Ángyán, Loos, and Mayer.¹ The more general delocalization index is, as both Fradera et al.² and Ángyán, Loos, and Mayer point out, invariant to unitary transformations, while the CM bond order definition, in which only the $\mu = \nu$ “diagonal terms” of eq 3 are kept, is not. However, as Ángyán et al. point out, on the basis of the population-localized orbitals Cioslowski and Mixon use, the neglected off-diagonal terms are small and for strictly localizable systems may be negligible. Furthermore, the localization procedure is *not* arbitrary and is well defined for a given basis set. One of its greatest practical advantages is that in its current implementation¹¹ the various bond orders are readily seen from the individual orbital populations.

Cioslowski and Mixon go on to define the ionicity¹² of molecular orbital μ (in their representation) involving atoms (basins) i and j as

$$i_{\mu}(i, j) = \frac{\langle \mu | \mu \rangle_i - \langle \mu | \mu \rangle_j}{\langle \mu | \mu \rangle_i + \langle \mu | \mu \rangle_j} \quad (7)$$

While $i_{\mu}(i, j)$ does not have a simple relationship to the corresponding covalent bond order $p_{cov, \mu}(i, j)$ for molecular orbital μ , the quantity $p_{ion, \mu}(i, j) \equiv i_{\mu}^2(i, j)$ does, where $p_{ion, \mu}(i, j)$ is our newly defined ionic bond order for orbital μ . Defining the denominator of eq 7 as $t_{\mu}(i, j)$, the total occupancy of molecular orbital μ in basins i and j , it is not difficult to show that

$$p_{ion, \mu}(i, j) \equiv i_{\mu}^2(i, j) = 1 - \frac{p_{cov, \mu}(i, j)}{t_{\mu}(i, j)^2} \quad (8)$$

which may also be written as

$$p_{ion, \mu}(i, j) \equiv i_{\mu}^2(i, j) = 1 - \frac{p_{cov, \mu}(i, j)}{p_{cov, \mu}^{\max}(i, j)} \quad (9)$$

since $t_{\mu}(i, j)^2$ is the maximum value $p_{cov, \mu}(i, j)$ can assume for the total occupancies $t_{\mu}(i, j) = \langle \mu | \mu \rangle_i + \langle \mu | \mu \rangle_j$, $p_{cov, \mu}^{\max}(i, j)$ acts as a scaling factor for the bond order; it will be unity when

virtually all the atomic occupancies of molecular orbital μ are contained in basins i and j and will also approach this value for a highly localized orbital.

The definition of ionic bond order given in eq 9 (and eq 8) is particularly simple, and its attractiveness lies in the fact that it fits in so naturally with the Cioslowski-Mixon definition of covalent bond order. Given a bonding orbital, the ratio of $p_{\text{cov}, \mu}(i, j)/p_{\text{cov}, \mu}^{\text{max}}(i, j)$ varies from (near) zero to unity as the ionic bond order varies from unity to zero. Because of the nature of the atomic orbitals, there will always be some overlap of orbitals into adjacent basins so $p_{\text{cov}, \mu}(i, j)$ can never actually be zero.

III. Details of the Calculations

The CM bond orders as well as the general optimizations and minimum-confirming frequency calculations were carried out in the B3LYP/6-311+G(d,p) approach^{13,14} with Gaussian 03.¹¹ In our tables the doubly occupied localized orbitals are listed by increasing negative kinetic energy; accordingly, core orbitals come near the top of the list and valence and lone pair orbitals near the bottom. Our characterization of the orbital type is based on a combination of the energy listing and our basic understanding of the constitution of core, valence, and lone pair orbitals.

IV. Results and Discussion

For the most part the examples we cite below are straightforward. To the extent a bond is covalent, that is, has a high covalent bond order, it is not ionic, that is, it has a small ionic bond order. Conversely, when a bond has a high ionic bond order, its covalent order will be small. However, before we exhibit a number of examples, we take a brief interlude to talk about some qualitative ideas of chemical bonding.

IV.1. An Interlude on Chemical Bonding. The application of the results expressed in eq 9 (or eq 8) requires some restraint as well as some understanding of what chemists mean when they refer to a chemical bond. We will discuss this generally here and show applications of this discussion in the material that follows.

We shall find that the Li 1s core orbital is spread slightly into the hydrogen atomic basin in LiH. We can, therefore, calculate both a (very small) covalent bond order and a corresponding ionic bond nearly equal to unity. But, we normally do not consider this as representing an ionic bond, basically because the two electrons occupying the Li 1s core both “belong” to the Li atom. The oxygen lone pairs in H₂CO have a slight spread into the C atomic basin and even a very small amount into the hydrogen atomic basins. Yet we do not characterize these interactions as constituting highly ionic chemical bonds, again because the two electrons involved in each of the two lone pair orbitals have their origins in the oxygen atom. The orbitals that dominate both CO bonding orbitals have contributions from the two hydrogen atomic basins. Accordingly, there can be defined a covalent bond order between oxygen and each hydrogen in these orbitals as well as an ionic bond order. Such secondary bonding is a result of the inability to completely localize any molecular orbital, but we do not characterize such interactions as

Table 1. Atomic Occupancies and Covalent (p_{cov}) and Ionic (p_{ion}) Bond Orders for LiH and LiF^a

A. LiH					
orbital	Li	H	orbital type	p_{cov}	p_{ion}
1	0.9962	0.0038	Li core	(0.0151	0.9849)
2	0.0556	0.9444	bond orbital	0.2100	0.7900
B. LiF					
orbital	Li	F	orbital type	p_{cov}	p_{ion}
1	0.0000	1.0000	F core		
2	0.0002	0.9998	F lone pair	(0.0008	0.9992)
3	0.9925	0.0075	Li core	(0.0298	0.9702)
4	0.0274	0.9726	bond orbital	0.1066	0.8934
5	0.0103	0.9897	F lone pair	(0.0408	0.9592)
6	0.0103	0.9897	F lone pair	(0.0408	0.9592)

^a Data for the core and lone pair orbitals are given in parentheses.

covalent or ionic. Do all these interactions contribute to the stability of the molecular species? Yes, otherwise they would not occur as they do. But it is not meaningful to talk about “bonds” in these cases; rather one should talk about stabilizing interactions of special kinds.

It is appropriate to discuss the covalent and ionic character of a bond when the orbital in question is part of the valence space, that is, where electrons from two or more dominant atomic species are involved. In the first few examples we discuss we include in the tables all the interactions to illustrate the points made above. But after this we shall include only the covalent and ionic character of bonds in the valence space.

IV.2. Examples of Ionic Bonds. Illustrative of highly ionic bonds are those in the lithium and sodium hydrides and fluorides and the FHF[−] anion.

Table 1 exhibits data for LiH and LiF and shows in parentheses contributions from core and lone pair orbitals, cases where, as discussed above, one should strictly speaking not talk about a chemical bond. The singular bonds in LiH and LiF are highly ionic with ionic bond orders of 0.7900 and 0.8934, respectively. Note in the two cases that small but finite covalent bond orders are determined for both core and lone pair orbitals, the latter being quite significant in LiF where three fluorine lone pairs are present. Note also that since we are dealing here with diatomics the sum of the covalent and ionic bond orders sum to unity.

The results for NaH and NaF shown in Table 2 are similar to those of the lithium analogues. Here again we show all calculated bond orders including core and lone pairs where we really cannot talk about chemical bonds. Interestingly, the bond in NaH is of equal covalent and ionic parts (as is KH, data not shown), but the bond in NaF is highly ionic, with an ionic bond order of 0.8453. In this regard since Li, Na, and K all have comparable electronegativities, it is a bit surprising that the covalent bond order of LiH is as small as it is.

Table 3 shows the various contributions to the covalent bond orders in these four molecules. Note that the large contribution by lone pairs in LiF causes the total covalent bond orders in LiH and LiF to be about the same. There is also a noticeable contribution by lone pairs in NaF, but the

Table 2. Atomic Occupancies and Covalent (p_{cov}) and Ionic (p_{ion}) Bond Orders for NaH and NaF^a

A. NaH					
orbital	Na	H	orbital type	p_{cov}	p_{ion}
1	1.0000	0.0000	Na $n = 1$ core		
2	0.9955	0.0046	Na $n = 2$ core	(0.0183	0.9817)
3	0.9989	0.0011	Na $n = 2$ core	(0.0044	0.9956)
4	0.9989	0.0011	Na $n = 2$ core	(0.0044	0.9956)
5	1.0000	0.0000	Na $n = 2$ core		
6	0.1494	0.8506	bond orbital	0.5083	0.4917

B. NaF					
orbital	Na	F	orbital type	p_{cov}	p_{ion}
1	1.0000	0.0000	Na $n = 1$ core		
2	0.0000	1.0000	F core		
3	0.9926	0.0074	Na $n = 2$ core	(0.0294	0.9706)
4	0.9982	0.0018	Na $n = 2$ core	(0.0072	0.9928)
5	0.9982	0.0018	Na $n = 2$ core	(0.0072	0.9928)
6	1.0000	0.0000	Na $n = 2$ core		
7	0.0008	0.9992	F lone pair	(0.0032	0.9968)
8	0.0403	0.9597	bond orbital	0.1547	0.8453
9	0.0087	0.9913	F lone pair	(0.0345	0.9655)
10	0.0087	0.9913	F lone pair	(0.0345	0.9655)

^a Data for the core and lone pair orbitals are given in parentheses.

Table 3. Contributions to the Total Covalent Bond Orders in LiH, LiF, NaH, and NaF from Core, Lone Pair, and Bond Orbitals

	LiH	LiF
Li core	0.0151	0.0298
F lone pairs		0.0824
bond	0.2100	0.1066
total	0.2251	0.2188

	NaH	NaF
Na core	0.0271	0.0438
F lone pairs		0.0722
bond	0.5083	0.1547
total	0.5354	0.2707

low bond contribution in NaF makes its total covalent bond order about half that of NaH.

The interesting case of the FHF⁻ anion is illustrated by the data in Table 4. Here all orbital occupancies are listed, but bond orders are only shown for orbitals 9 and 10 which represent the chemical bonds in this system. Note that these are basically two-center two-electron bonds; that is, the CM decomposition does not reveal any three-center bonds which might have been present here. The ionic bond order of the two bonds is quite high showing that one can represent this system basically as F⁻H⁺F⁻.

IV.3. Some Examples of Typical Covalent Bonds.

Illustrative of typical covalently bonded but polar bonds are H₂CO and HNCH₂ whose data are given in Tables 5 and 6. The CH and CO bonds in formaldehyde are shown as orbitals 7,8 and 4,6, respectively. As expected the CH bonds are nearly pure covalent bonds, while those between C and O are polar, exhibiting ionic bond orders of 0.3792 and 0.2313. Because of the polarity of the CO bonds, the covalent character of these sums to 1.3566, considerably less than 2.0 that would be expected for a pure covalent double bond.

Table 4. Atomic Occupancies, Covalent (p_{cov}) and Ionic (p_{ion}) Bond Orders, and the Covalent Bond Order Matrix for the Linear FHF Anion^a

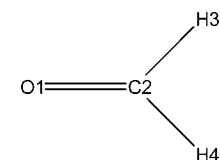
(F1 — H2 — F3)⁻

A. Orbital Occupancies							
orbital	F1	H2	F3	orbital type	p_{cov}	p_{ion}	
1	0.0000	0.0000	1.0000	F3 core			
2	1.0000	0.0000	0.0000	F1 core			
3	0.0002	0.0001	0.9996	F3 lone pair			
4	0.9996	0.0001	0.0002	F1 lone pair			
5	0.0036	0.0042	0.9922	F3 lone pair			
6	0.9922	0.0042	0.0036	F1 lone pair			
7	0.0036	0.0042	0.9922	F3 lone pair			
8	0.9922	0.0042	0.0036	F1 lone pair			
9	0.9066	0.0726	0.0208	F1H2 bond	0.2633	0.7254	
10	0.0208	0.0726	0.9066	H2F3 bond	0.2633	0.7254	

B. Covalent Bond Order Matrix			
	F1	H2	F3
F1	9.5806		
H2	0.3033	0.0212	
F3	0.2110	0.3033	9.5806

^a The primary bond data are given in bold.

Table 5. Orbital Occupancies, Covalent (p_{cov}) and Ionic (p_{ion}) Bond Orders for the Indicated Bonds, and the Covalent Bond Order Matrix for H₂CO^a

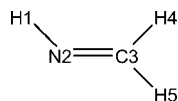


A. Orbital Occupancies							
orbital	O1	C2	H3	H4	type	p_{cov}	p_{ion}
1	1.0000	0.0000	0.0000	0.0000	O core		
2	0.0008	0.9992	0.0000	0.0000	C core		
3	0.9989	0.0008	0.0002	0.0002	O lone pair		
4	0.8015	0.1906	0.0040	0.0040	OC bond	0.6111	0.3792
5	0.9448	0.0338	0.0107	0.0107	O lone pair		
6	0.7292	0.2556	0.0076	0.0076	OC bond	0.7455	0.2313
7	0.0244	0.5104	0.4553	0.0099	CH bond	0.9295	0.0033
8	0.0244	0.5104	0.0099	0.4553	CH bond	0.9295	0.0033

B. Covalent Bond Order Matrix				
	O1	C2	H3	H4
O1	8.1318			
C2	1.5901	3.2444		
H3	0.1214	0.9619	0.4152	
H4	0.1214	0.9619	0.0368	0.4152

^a The primary bond data are indicated in bold.

The covalent bond orders for the two CC bonds in ethylene (data not shown) are 0.9513 and 0.8832 summing to 1.8345, and with zero ionic bond order due to the molecular symmetry. The covalent and ionic bond orders for the CO and OH bonds in ethanol (data not shown) are 0.6959, 0.2726 and 0.6525, 0.3288, respectively.

Table 6. Atomic Occupancies, Covalent (p_{cov}) and Ionic (p_{ion}) Bond Orders for the Indicated Bonds, and the Covalent Bond Order Matrix for HNCH_2^a 

A. Atomic Occupancies of Localized Orbitals								
orbital	H1	N2	C3	H4	H5	orbital type	p_{cov}	p_{ion}
1	0.0000	1.0000	0.0000	0.0000	0.0000	N core		
2	0.0000	0.0003	0.9997	0.0000	0.0000	C core		
3	0.0069	0.9749	0.0110	0.0041	0.0031	N lone pair		
4	0.0051	0.7197	0.2637	0.0078	0.0036	NC bond	0.7591	0.2150
5	0.3139	0.6639	0.0162	0.0023	0.0038	H1N bond	0.8836	0.1281
6	0.0087	0.6276	0.3412	0.0112	0.0113	NC bond	0.8565	0.0874
7	0.0029	0.0206	0.5139	0.0088	0.4538	CH5 bond	0.9328	0.0039
8	0.0019	0.0189	0.5120	0.4590	0.0082	CH4 bond	0.9400	0.0030

B. Covalent Bond Orders					
	H1	N2	C3	H4	H5
H1	0.1974				
N2	0.8976	6.6078			
C3	0.0477	1.7834	3.4240		
H4	0.0071	0.1081	0.9820	0.4220	
H5	0.0106	0.0988	0.9694	0.0318	0.4124

^a The primary bond data are indicated in bold.

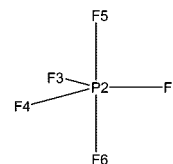
Methylene imine, HNCH_2 , is an interesting molecule in that a contribution to N2C3 covalent bond order is made by the nitrogen lone pair. As the data in Table 6 show, both the HN and NC bonds are polar, while the CH bonds are virtually pure covalent.

IV.4. Two Unusual Cases and Limitations of the Method. Finally we treat the unusual (hypervalent) PF_5 and diborane molecules. Table 7 contains the dominant bond occupancies for these two cases.

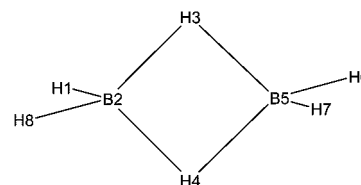
The axial and equatorial bonds in PF_5 are very similar, having similar covalent and ionic bond orders and (optimized) bond distances as well, 1.6051 and 1.5709 Å, respectively. Notably there are no three center bonds in the CM localized set of orbitals.

Diborane is a different case and illustrates one of the limitations of specifying bond orders of either type. While the external BH bonds are two-center dominated (orbital 7), the internal BHB bonds (illustrated by orbital 3) are three-center in character. Our formulas do not easily reconcile how one is to characterize the covalent and ionic character of such bonds. There is obviously covalent character, and the bond, while not polar, is polarized toward the bridging hydrogen. Here we simply take the average of the two two-center fragment data (both the same due to the molecular symmetry) to characterize this bond.

The situation in diborane typifies the general failure of the CM localization process to always provide two-center dominant localized orbitals. Indeed, Cioslowski and Mixon³ note that unique localized orbitals are generally found when one can associate with the molecule a single, dominant Lewis structure. This is not the case for highly symmetric molecules like benzene or the cyclopentadienyl anion which do not converge in the CM treatment.

Table 7. Orbital Occupancies and Their Covalent (p_{cov}) and Ionic (p_{ion}) Bond Orders for the Two Classes of Bonds in PF_5 and the External and Internal BH and BHB Bonds in Diborane^{a,b}A. PF_5 

	F1	P2	F3	F4	F5	F6	p_{cov}	p_{ion}
27	0.8629	0.1091	0.0030	0.0030	0.0110	0.0110	0.3766	0.6014
30	0.0121	0.1003	0.0122	0.0122	0.0002	0.8630	0.3462	0.6269

B. $\text{H}_2\text{BH}_2\text{BH}_2$ (diborane)

	H1	B2	H3	H4	B5	H6	H7	H8
3	0.0136	0.1089	0.6947	0.0332	0.1089	0.0136	0.0136	0.0136
7	0.7391	0.1980	0.0191	0.0191	0.0038	0.0013	0.0022	0.0176

orbital	p_{cov}	p_{ion}
3	0.3026 ^a	0.5314 ^a
7	0.5854	0.3334

^a Average of the two-center fragments in orbital 3. ^b The dominant bond data are given in bold.

V. Summary

Taking the square of the bond ionicity, $i_{\mu}^2(i,j)$, for molecular orbital μ in the localized orbital representation of Cisolowski and Mixon³ as an ionic bond order, one finds a simple and natural relation between the scaled covalent bond order, $p_{\text{cov},\mu}(i,j)/p_{\text{cov},\mu}^{\text{max}}(i,j)$, and the ionic bond order, $p_{\text{ion},\mu}(i,j)$. Their sum is unity; to the extent that an orbital is covalent, it is not ionic, and to the extent that it is ionic it is not covalent. A number of examples have been presented using the B3LYP/6-311+G(d,p) density functional approach as well as limitations of the method.

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