

Continuity of Bond Order*

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To preserve the continuity of a recent bond order concept [1], the Mulliken overlap criterion for bonding and antibonding is replaced by a vector projection weighting procedure. The consequences of this change are discussed in applications to selected diatomics and polyatomics.

Key words: Bond order

1. Introduction

We recently introduced a new bond order concept which was based on diagonalization of the two-center parts of the density matrix [1]. We showed that the bond order between two atoms can be obtained as a sum of eigenvalues of a resulting eigenvalue equation. We could prove that the eigenvalues appear in pairs $\pm \lambda_i$ for even and odd numbers of basis orbitals and that in the latter case at least one eigenvalue is zero. Vanishing eigenvalues appear always when the number of basis orbitals on each of the two atoms is different. This accounts for non-bonding contributions to the total bond order. To distinguish between bonding and antibonding contributions to the total bond order, the positive and negative pairs of non-vanishing eigenvalues seemed appropriate. We used the Mulliken criterion [2] of positive overlap between the hybrids on the two atoms for bonding and negative overlap for antibonding. The positive eigenvalues were multiplied with $+1$ when the accompanying bond order orbitals had positive overlap and with -1 when they had negative overlap. The total bond order between two atoms was then a sum of bonding and antibonding contributions. Unfortunately we discovered that

Dedicated to Professor H. Hartmann on his 65th birthday.

discontinuities arose when bonding orbitals could become antibonding and *vice versa* with changes in geometry or basis set.

This is because the nodes of the density matrix are not necessarily accompanied by nodes in the overlap of the respective bond order orbitals. In the next section it is described how the discontinuities can be avoided by replacement of Mulliken's overlap criterion for bonding and antibonding by a vector projection technique. In the last section we compare the results for the two criteria in a few relevant cases.

2. Modification of Method

Bond order orbitals are eigenfunctions of those two-center parts of the density matrix which refer to the two atoms A and B under consideration. They are given as a sum of hybrids [3],

$$b_i = g_i + h_i = \bar{g}_i + \bar{h}_i. \quad (2.1)$$

g_i and h_i are combinations of Schmidt and Löwdin orthogonalized basis orbitals on atoms A and B. \bar{g}_i and \bar{h}_i are the respective orbitals after removal of the Löwdin orthogonalization. The total bond order was previously [1]

$$P_{AB} = \sum_i \lambda_i \text{sign}(S_{\bar{g}_i \bar{h}_i}), \quad (2.2)$$

where λ_i is the eigenvalue belonging to b_i and S the overlap integral over non-orthogonal orbitals. A better form of the bond order to preserve continuity would be

$$P_{AB} = \sum_i \lambda_i \cos \varphi_i. \quad (2.3)$$

(2.3) contains (2.2) formally as a special case. However, we want to drop the overlap criterion completely since overlap does not appear explicitly in the Löwdin orthogonalized basis. We suggest that we can consider the g_i and h_i as linear combinations of basis vectors in a Hilbert space. Then a natural definition for $\cos \varphi_i$ would be by the scalar product

$$\cos \varphi_i = \frac{\mathbf{g}_i \cdot \mathbf{h}_i}{|\mathbf{g}_i| \cdot |\mathbf{h}_i|}. \quad (2.4)$$

φ_i is the angle between the two bond order vectors which compose the bond order orbital. Each component is attached to one of the atoms. We now look whether these vectors are parallel, antiparallel or form any angle in between these two situations. Let us take as an example the description of the π -system in a minimal basis set. The π MO is also a π bond order orbital and has the form:

$$\begin{aligned} b_\pi &= \frac{1}{\sqrt{2}} (2p\pi_A + 2p\pi_B) \\ &= \frac{1}{\sqrt{2}} 2p\pi_A + \frac{1}{\sqrt{2}} 2p\pi_B. \end{aligned}$$

In this case it follows that the vectors are parallel regardless of their orbital exponent so that

$$\cos \varphi_i = \frac{\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}}}{\frac{1}{\sqrt{2}} \cdot \frac{1}{\sqrt{2}}} = 1.$$

In the more general case we assume for convenience that on each atom in a molecule the same number of equivalent orbitals is present in the basis set. The projection is then particularly simple. What to do in cases where such an assumption is not feasible is demonstrated in the case of binding between an atom X and a hydrogen atom H. In this case we could use a reference orbital from a reference compound which is to yield a weighting factor 1 in the reference compound

$$b = \frac{1}{\sqrt{2}}(g_X + 1s_H),$$

$$\cos \varphi_{RH} = g_R \cdot 1s_H = 1.$$

The cosine between vector g_X and g_H is then calculated as

$$\cos \varphi_{XH} = g_R \cdot g_X \tag{2.5}$$

g_X and $1s_H$ are normalized. We suggest that g_R is the sp^3 hybrid orbital. This orbital is very closely the carbon part of the bond order orbital of CH_4 . This choice is not so arbitrary if we consider that the bond order between C and H in CH_4 is practically 1, as we shall see below.

3. Application

To demonstrate the advantage of the modification in the weighting of the bond order eigenvalues, we use SCF wavefunctions generated by a reliable semiempirical MO method for the ground state. A new version SINDO1¹ of a previously suggested semiempirical MO method [4] seemed appropriate since test results on over 100 molecules of first-row atoms showed an accuracy as good as or better than MINDO3. In particular bond angles were improved.

In Tables 1 and 2 we compare bond orders for homo- and heteropolar bonds. The molecules cover a representative range of single and multiple bonds with small and large polarity. σ and π contributions to the total bond order are defined in local coordinate systems. From these tables the differences in total bond order between the two weighting procedures is small or zero in most cases. The largest differences occur in molecules like C_2H , BeO, LiF where the 2 σ contribution weighted with the sign of the overlap is positive whereas the vector projection gives a negative value. In Table 3 hydride bond orders are compared. Differences occur only in LiH and BeH. The change is most pronounced in LiH where the bond order orbital is

¹ A preliminary account was presented by Dr. N. Nanda and the author at the 14. Symposium für Theoretische Chemie, Innsbruck, 19–21 September 1978.

Table 1. Bond orders and their components with different weighting factors for XX bonds^a

Molecule	Bond length		Weighted eigenvalues with Mulliken criterion					Weighted eigenvalues with vector projection criterion					Total bond order
	calc.	exp.	1 σ	2 σ	πx	πy	Total bond order	1 σ	2 σ	πx	πy	Total bond order	
C ₂ H	1.221	1.207	0.938	0.130	0.946	0.946	2.960	0.932	-0.129	0.946	0.946	2.695	
C ₂ H ₂	1.209	1.203	0.995	-0.053	1.000	1.000	2.942	-0.995	-0.053	1.000	1.000	2.942	
C ₂ H ₄	1.320	1.337	0.999	-0.040	1.000	0.208	2.167	0.999	-0.040	1.000	0.208	2.167	
C ₂ H ₆	1.528	1.536	1.000	-0.030	0.142	0.142	1.254	0.9997	-0.030	0.142	0.142	1.254	
C ₆ H ₁₂	1.556	1.536	0.984	-0.044	0.131	0.129	1.200	0.983	-0.043	0.130	0.129	1.199	
N ₂ H ₂	1.209	—	1.000*	0.017*	1.000	0.198*	2.215	0.998*	0.015*	1.000	0.174*	2.187	
N ₂ H ₄	1.426	1.449	0.999*	-0.040*	0.138*	0.085*	1.182	0.993*	-0.028*	0.134*	0.058*	1.157	
HN ₃	1.131	1.133	0.954*	-0.044*	0.905	0.971*	2.786	0.936*	-0.043*	0.905	0.956*	2.754	
H ₂ O ₂	1.356	1.237	0.818*	-0.101	0.424	0.260*	1.401	0.693*	-0.067*	0.424	0.211*	1.261	
O ₃	1.365	1.475	0.999*	0.000*	0.083	-0.081*	1.001	0.996	0.000	0.083	-0.009	1.070	
B ₂ H ₆	1.256	1.278	0.943*	0.000*	0.705	0.112*	1.760	0.923*	0.000*	0.705	0.067*	1.695	
	1.868	1.775	0.527	-0.029	0.387	0.112	0.997	0.527	-0.029	0.387	0.387	0.997	

^a Values marked with asterisk belong to orbitals which are mixtures of σ and π

Table 2. Bond orders and their components with different weighting factors for XY bonds^a

Molecule	Bond length		Weighted eigenvalues with Mulliken criterion				Total bond order	Weighted eigenvalues with vector projection criterion				Total bond order
	calc.	exp.	1σ	2σ	πx	πy		1σ	2σ	πx	πy	
CO	1.150	1.128	0.963	0.000	0.900	0.900	2.763	0.957	0.000	0.900	0.900	2.757
HCO	1.186	1.198	0.963*	-0.049*	0.900	0.572*	2.392	0.962*	-0.047*	0.906	0.560*	2.381
CO ₂	1.202	1.162	0.980	-0.087	0.658	0.658	2.209	0.894	-0.079	0.658	0.658	2.131
H ₂ CO	1.213	1.208	0.995	-0.058	0.964	0.343	2.244	0.976	-0.057	0.964	0.343	2.224
H ₃ COH	1.389	1.425	0.985*	-0.052*	0.194	0.155*	1.282	0.980*	-0.051*	0.194	0.153*	1.276
NO	1.152	1.151	0.989	0.000	0.963	0.466	2.418	0.989	0.000	0.963	0.466	2.417
NO ₂	1.214	1.193	0.916*	-0.056*	0.694	0.441*	1.995	0.900*	-0.055*	0.694	0.436*	1.975
HNO	1.194	1.212	0.998*	0.000*	0.995	0.210*	2.203	0.997*	0.000*	0.995	0.153*	2.145
H ₃ NO	1.382	—	0.866	-0.075	0.213	0.213	1.217	0.803	-0.070	0.213	0.213	1.159
NH ₂ CN	1.170	1.178	0.974*	-0.131*	0.970*	0.927*	2.740	0.855*	-0.115*	0.970*	0.927*	2.637
	1.357	1.328	0.976*	-0.058*	0.317	0.200*	1.435	0.965*	-0.057*	0.317	0.200*	1.425
LiF	1.540	1.563	0.664	0.186	0.340	0.340	1.530	0.660	-0.185	0.340	0.340	1.155
BF	1.276	1.262	0.833	0.000	0.537	0.537	1.907	0.808	0.000	0.537	0.537	1.882
CF ₄	1.336	1.321	0.919	-0.056	0.171	0.171	1.185	0.917	-0.056	0.171	0.171	1.183
NF ₃	1.335	1.365	0.966*	0.000*	0.136*	0.133*	1.235	0.961*	0.000*	0.109*	0.128*	1.198
BeO	1.348	1.331	0.991	0.430	0.697	0.697	2.815	0.540	-0.234	0.697	0.697	1.700

^a Values marked with asterisk belong to orbitals which are mixtures of σ and π

Table 3. Bond orders and their components with different weighting factors for XH bonds

Molecule	Bond length		Total bond order with	
	calc.	exp.	Mulliken criterion	Vector projection criterion
LiH	1.570	1.595	0.900	0.789
BeH	1.326	1.343	0.920	0.862
BH	1.215	1.233	0.989	0.989
CH	1.082	1.128	0.998	0.998
NH	1.022	1.038	0.990	0.990
OH	0.982	0.971	0.978	0.978
FH	0.921	0.917	0.954	0.954
C ₂ H ₂	1.038	1.060	0.993	0.943
C ₂ H ₄	1.088	1.086	0.988	0.982
C ₂ H ₆	1.113	1.091	0.993	0.993
CH ₄	1.111	1.094	0.999	0.999
NH ₃	1.033	1.012	0.993	0.992
H ₂ O	0.979	0.957	0.978	0.978

composed of hybrid on Li which has much more *s* character than the sp^8 reference orbital.

Whereas a decision for the modification might not seem compelling from these tables, it will be from the following figures. In Fig. 1 we present the variation of the bond order with varying CC bond length in acetylene. With the Mulliken overlap criterion it is possible that the antibonding 2σ contribution becomes bonding with increasing distance. The result is a discontinuity in the bond order. Since we did not try to locate the exact distance at which the change of overlap occurs the figure shows only the rapid but unjustified increase in the region between 1.2 and 1.3 Å. The vector projection result is smooth. Figure 2 shows a similar discrepancy for the variation of the rotation angle of H₂O₂ when the overlap criterion is used. Again the vector weighting technique gives an acceptable result.

4. Conclusion

The criterion for bonding and antibonding contributions to the total bond order had to be modified to preserve continuity in critical cases. The overlap criterion introduced by Mulliken was replaced by a vector projection technique which allows a continuous change from bonding to antibonding. It is based on the following steps: (1) We assume that the SCF or CI wavefunctions are obtained by LCAO MO's. The same basis orbitals are used on all atoms of the same row. (2) The Schmidt orthogonalized orbitals on one atom are considered as orthogonal vectors in a Hilbert space. The basis orbitals on other atoms can then be considered as parallel or orthogonal to the first atomic set. Orbital exponents are disregarded

ACETYLENE

△ - BOND ORDER (OVERLAP)
+ - BOND ORDER (PROJECTION)

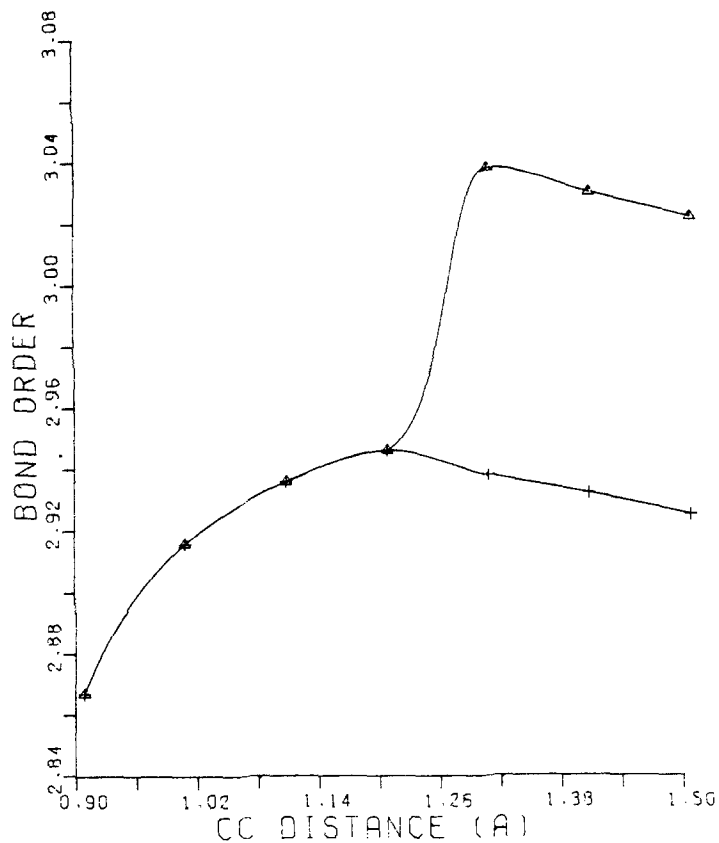


Fig. 1. Bond order dependence on CC bond length in acetylene with overlap and projection criterion

in this consideration. For bonds between atoms of different rows reference orbitals can be defined on which projection of the actual hybrids is performed. (3) The Löwdin orthogonalization is performed and the projection for two vectors referring to different atoms calculated in this basis set.

The advantage of the present procedure was demonstrated for equilibrium and non-equilibrium situations of selected molecules.

H2O2

△ - BOND ORDER (OVERLAP)
 + - BOND ORDER (PROJECTION)

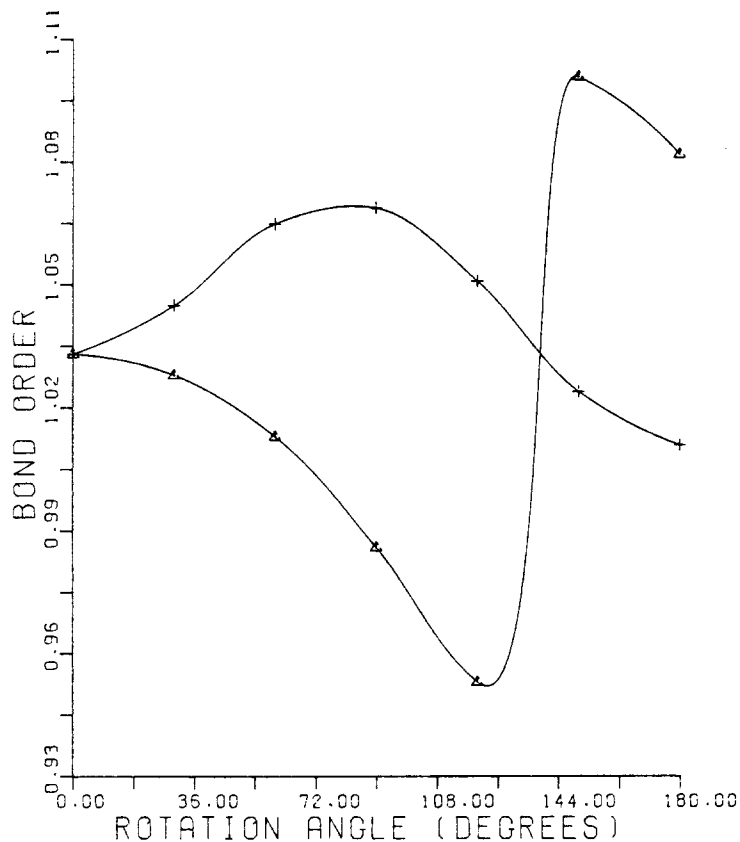


Fig. 2. Bond order dependence on HOOH dihedral angle in H_2O_2 with overlap and projection criterion

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