A Maximum Bond Order Principle[†]

Karl Jug

Contribution from Theoretische Chemie, Technische Universität Hannover.
Hannover. Germany. Received June 16, 1976

Abstract: A maximum bond order principle is introduced in the LCAO formalism to serve as a generalization of the chemist's idea of single and multiple bonds. It is based on a sum of hybrid pair contributions from each atom pair considered. By application of the variation principle to these hybrid pairs, the bond order for each pair of atoms appears as a sum of eigenvalues of the two-center part of the related density matrix. The definition is general enough to include antibonding effects and is applicable to any size of LCAO basis sets as well as open shell and CI wave functions. The method contains Coulson's π-electron bond order as a special case, but differs from Mulliken's in various aspects. Several applications with SINDO wave functions to exotic diatomics, hydrogen bonds, bond lengths, and reactions are presented.

I. Introduction

The concept of bond order can be found in many elementary textbooks. It generally relates to valency multiplicity between atoms in molecules. It is helpful to think in terms of single, double, and triple bonds in F_2, O_2, N_2, ethane, ethylene, or acetylene. Molecular orbital theory allows us to use this outgrowth of chemical intuition in a more systematic way. Textbooks emphasize the following relations between bond orders and (a) overlap populations in the bonding region,[1] (b) bond strengths in terms of energy contribution to the bonding,[1,2] (c) bond lengths.[3,4] A closer look reveals, however, that there are only three types of bonds considered: the homonuclear diatomic bond, the π bond in conjugated systems, and the pure hybridized σ bonds of sp, sp², or sp³ type. The π-bond order in conjugated systems was introduced by Coulson[5] and based on the presence of only one AO per atom and the assumption that the AOs $\{\lambda\}$ are orthogonalized:

$$P^\lambda = C^\lambda (C^\lambda)^\dagger$$

Later Chirgwin and Coulson[6] modified this concept to include nonorthogonal AOs $\{\chi\}$ on the atoms:

$$N^\chi = \frac{1}{2}(P^\chi S + S P^\chi)$$

with

$$P^\chi = C^\chi (C^\chi)^\dagger$$

The diagonal terms of N^χ are Mulliken's gross atomic charges.[7] Let us assume that the basis sets centered on each atom are orthogonal; if they are not they can be Schmidt orthogonalized. From all possible orthogonalizations of orbitals on different centers the Löwdin orthogonalization[8] appears most appropriate since it changes the AO's character as little as possible. It relates P^λ and P^χ in the following way:

$$P^\lambda = S^{1/2} P^\chi S^{1/2}$$

It follows that

$$N^\chi = P^\lambda \text{ if } [P^\chi, S] = 0$$

Several years later, Mulliken[9] tried to remove the restriction of a single AO on each atom. His paper contains several alternatives which are originally discussed only in the case of diatomics. His most advanced suggestion is for an orthogonalized AO basis and takes the bond order as the sum of all two-center elements of the density matrix. This definition does not conform with our concept that a single bond has bond order one, double bond two, etc. Rather, single bonds can have bond

orders close to two, double bonds close to three, etc. But the serious objection to Mulliken's definition is that it is *not* invariant under coordinate transformation. Thus any application of it in polyatomics has to be regarded with much caution. A further drawback is the fact that his discovery that σ bond orders might deviate from unity prompted him to rescale them to one. In the following section we suggest an approach to handle the bond orders in AH and AB fragments in minimal basis sets.

II. The Extremum Principle for Bond Orders Introduced in AH and AB Fragments

In the case of an AH bond with a 1s AO on atom H and 2s, 2p AOs on atom A the resulting σ bond is given by the contributions of all occupied MOs involving $1s_H$, $2s_A$, and $2p_A$ orbitals, the latter being directed toward the H atom. The LCAO bond order can now be defined as a two-center element of the density matrix, or charge and bond order matrix called by Coulson, involving a hybrid h on A and s′ on H.

$$P_{AH} = P_{hs'}$$

The orthonormalized hybrid has the form

$$h = a s_A + \sqrt{1 - a^2}\, p_A \tag{2.1}$$

so that the bond order appears as

$$
\begin{aligned}
P_{AH} &= \langle (a s_A + \sqrt{1 - a^2}\, p_A) | P_{op} | s'_H \rangle \\
&= a P_{ss'} + \sqrt{1 - a^2}\, P_{ps'}
\end{aligned}
\tag{2.2}
$$

where P_{op} is the density operator.

It is apparent that the bond order is not only dependent on $P_{ss'}$ and $P_{ps'}$ but also on a, i.e., the choice of the hybrid on A. Whereas $P_{ss'}$ and $P_{ps'}$ can be determined by an SCF calculation, there is no natural choice of h. To think in terms of sp, sp², and sp³ hybrids would be inappropriate in many situations, for instance in hydrogen bonds, and quantum chemistry deals with continuous mixing of s and p anyway. It seems suggestive to consider the bond formation between the atoms as a situation where the largest bond orders possible are obtained. We therefore determine a with given $P_{ss'}$ and $P_{pp'}$ by

$$\frac{dP_{AH}}{da} = 0 \tag{2.3}$$

$$P_{ss'} - \frac{a}{\sqrt{1 - a^2}} P_{ps'} = 0 \tag{2.4}$$

$$a = \frac{\dfrac{P_{ss'}}{P_{ps'}}}{\sqrt{1 + \left(\dfrac{P_{ss'}}{P_{ps'}}\right)^2}} \tag{2.5}$$

Finally P_{AH} is evaluated by (2.2) and (2.5) as

$$P_{AH} = P_{ps'} \sqrt{1 + \left(\frac{P_{ss'}}{P_{ps'}}\right)^2}$$

$$= \pm \sqrt{P_{ss'}^2 + P_{ps'}^2} \qquad (2.6)$$

The plus sign refers to $P_{ps'} > 0$ and the minus sign to $P_{ps'} < 0$. We can actually check whether we have a maximum or minimum by looking at the second derivative

$$\frac{d^2 P_{AH}}{da^2} = -\frac{1}{(1-a^2)^{3/2}} P_{ps'}$$

and find (2.5) confirmed: a maximum for $P_{ps'} > 0$ and a minimum for $P_{ps'} < 0$. We see that it is possible to obtain positive and negative orders. So the approach is general enough to include both bonding and antibonding situations. But the criterion for the plus or minus sign in (2.6) will have to be modified in the next section, when we allow for a more general form of the hybrids than (2.1) implies. In the case of an AB bond the situation is different. Several orthogonal hybrids can be constructed on each atom. We suggest that hybrids of the same form shall be coupled through the density operator P_{op}. The bond order will take the form

$$P_{AB} = \langle (as_A + \sqrt{1-a^2}\sigma_A)|P_{op}|(bs_{B'} + \sqrt{1-b^2}\sigma_B)\rangle$$

$$+ \langle(-\sqrt{1-a^2}\,s_A + a\sigma_A)|P_{op}|(-\sqrt{1-b^2}\,s_{B'} + b\sigma_B)\rangle$$

$$+ \langle\pi_A|P_{op}|\pi_B\rangle + \langle\bar{\pi}_A|P_{op}|\bar{\pi}_B\rangle$$

$$= (ab + \sqrt{1-a^2}\sqrt{1-b^2})(P_{ss'} + P_{\sigma\sigma'})$$

$$+ (b\sqrt{1-a^2} - a\sqrt{1-b^2})(P_{\sigma s'} - P_{s\sigma'})$$

$$+ P_{\pi\pi'} + P_{\bar{\pi}\bar{\pi}'} \qquad (2.7)$$

For $a = b = 1$, this would be the sum of the diagonal elements of the two-center part of the density matrix. With the above form we allow for the possibility of $s_A\sigma_B$ bonds in heteromolecules. The condition for a maximum of P_{AB} is

$$\frac{\partial P_{AB}}{\partial a} = \frac{\partial P_{AB}}{\partial b} = 0 \qquad (2.8)$$

The procedure of solution for a and b is technically rather more involved than in the case of P_{AH}, so we present only the final result:

$$P_{AB} = \pm \sqrt{(P_{ss'} \pm P_{\sigma\sigma'})^2 + (P_{\sigma s'} \mp P_{s\sigma'})^2}$$
$$+ P_{\pi\pi'} + P_{\bar{\pi}\bar{\pi}'} \qquad (2.9)$$

Before we proceed to the general method, we want to prove that the sum over *all* two-center density matrix elements is not invariant under transformation of the coordinate axes, hence unsuitable as a bond order concept. Let

$$P_{AH} = \langle s|P_{op}|s_H\rangle + \langle x|P_{op}|s_H\rangle$$

$$+ \langle y|P_{op}|s_H\rangle + \langle z|P_{op}|s_H\rangle$$

$$= P_{sH} + P_{xH} + P_{yH} + P_{zH}$$

If a new coordinate system is generated through rotation of x and y axes about the z axis by an angle φ, P_{AH} would be dependent on the angle of rotation:

$$P_{AH} = P_{sH} + (\cos\varphi + \sin\varphi)P_{x'H}$$
$$+ (\cos\varphi - \sin\varphi)P_{y'H} + P_{z'H}$$

This fact disqualifies Mulliken's definition as a suitable alternative in molecules with less symmetry than linear molecules have. Only in the latter case we find $P_{x'H} = P_{y'H} = 0$ when the z axis is taken as the symmetry axis.

There are few further simple examples in which an analytical form for the bond order can be developed. The next section

will attack the problem more generally in matrix form and by means of eigenvalue equations.

III. The General Method

Let $A = (a_1, \ldots, a_m)$ and $B = (b_1, \ldots, b_n)$ be AO basis sets on atoms A and B. The basis sets are supposed to be Schmidt orthonormalized on each atom and subsequently Löwdin orthonormalized with respect to the whole set. The size of the two sets on A and B can be different. We construct now orthogonal hybrids G on A and H on B:

$$G = AT$$
$$H = BU \qquad (3.1)$$

with

$$\tilde{G}G = \tilde{T}\tilde{A}AT = I$$
$$\tilde{H}H = \tilde{U}\tilde{B}BU = I'$$

For orthogonal basis sets

$$\tilde{T}T = I$$
$$\tilde{U}U = I' \qquad (3.2)$$

It seems suggestive to define a bond order P_{AB} between atoms A and B by an *extremum principle*. The bonds between two atoms are supposed to be formed by maximum positive bond orders for a bonding situation and maximum negative bond orders for antibonding situations. This can be accomplished by selecting pairs $\{g_i, h_i\}$ of hybrids on A and B and maximizing the sum of pairs $P_{g_ih_i}$. The number of pairs to be formed is $\min(m, n)$. The bond order is now defined as the maximum of the trace of elements of G and H coupled through the density operator P_{op}:

$$P_{AB} = \text{Tr}(\tilde{G}P_{op}H)$$

$$= \text{Tr}(\tilde{T}\tilde{A}P_{op}BU)$$

$$= \text{Tr}(\tilde{T}PU) \qquad (3.3)$$

with

$$\text{Tr} = \sum_i^{\min(m,n)}$$

P is the two-center part of the density matrix of A and B over the basis OAOs. We determine the maximum of P_{AB} subject to the orthogonality conditions (3.2). For this purpose we define a functional

$$P_{AB}' = P_{AB} + \text{Tr}[(I - \tilde{T}T)\Lambda] + \text{Tr}[\Lambda'(I' - \tilde{U}U)] \quad (3.4)$$

where Λ and Λ' are Lagrange multipliers. The extremum conditions are

$$\frac{\partial P_{AB}'}{\partial \tilde{T}} = \frac{\partial P_{AB}'}{\partial U} = 0 \qquad (3.5)$$

This abbreviated form means that the derivatives have to be taken with respect to all elements of $\tilde{T}$ and U. We obtain the following set of equations:

$$PU - T(\Lambda + \tilde{\Lambda}) = 0$$
$$\tilde{T}P - (\Lambda' + \tilde{\Lambda}')\tilde{U} = 0 \qquad (3.6)$$

Since the trace runs only to $\min(m, n)$, we can ignore those parts of the matrices exceeding this size or fill in zeros to make them compatible. If the first equation is multiplied by $\tilde{T}$ from the left and the second equation multiplied by U from the right, it immediately follows that

$$P_{AB} = \text{Tr}(\Lambda + \tilde{\Lambda}) = \text{Tr}(\Lambda' + \tilde{\Lambda}') \qquad (3.7)$$

We now diagonalize $\Lambda + \tilde{\Lambda}$ by an orthogonal transformation

$$T = CX$$

$$U = C'Y$$

with

$$X(\Lambda + \tilde{\Lambda})\tilde{Y} = \Lambda_D \quad (3.8)$$

Λ_D is a diagonal matrix. It follows that (3.6) will be cast by (3.8) in the form

$$PC' - C\Lambda_D = 0$$

$$\tilde{C}P - \Lambda'_D\tilde{C}' = 0 \quad (3.9)$$

which can be written as

$$PC_i' - \lambda_iC_i = 0$$

$$\tilde{P}C_i - \lambda_iC_i' = 0 \quad (3.10)$$

An alternative presentation of these equations is the following matrix form:

$$\left(\frac{-\Lambda_D}{\tilde{P}}\Bigg|\frac{P}{-\Lambda_D'}\right)\left(\frac{C_o}{C_o'}\Bigg|\frac{C_u}{C_u'}\right) = 0 \quad (3.11)$$

$\{C_o, C_o'\}$ are occupied, $\{C_u, C_u'\}$ unoccupied hybrid pairs. It has the advantage to be generally valid for rectangular P matrices, since the total coefficient matrix always has the square form. Its solutions are given by the usual condition that the coefficient determinant of (3.11) vanishes:

$$|\overline{P}_{i_A/_B}(1 - \delta_{AB}) - \lambda_i\delta_{ij}| = 0 \quad (3.12)$$

Here $\overline{P}_{i_A/_B}$ means the totality of density matrix elements referring to atoms A and B. The single-center elements are eliminated by the factor $(1 - \delta_{AB})$. The two-center elements reduce to P and $\tilde{P}$, respectively. Since (3.7) will be converted by (3.8) into its final form

$$P_{AB} = \text{Tr } \Lambda_D \quad (3.13)$$

this means that the bond order appears as the sum of eigenvalues of the two-center part of the density matrix of the two atoms A and B.

If we cast (3.10) in operator form, we obtain

$$P_{op}H = G\Lambda_D$$

or

$$P_{op}h_i = \lambda_ig_i \quad (3.14)$$

There are apparent similarities of this equation with the eigenvalue equations of the energy, in particular with the derivation of the SCF equation.

From (3.12) we will prove now two important properties of the eigenvalues. Considering that Λ_D is diagonal (3.12) can be evaluated in the form when we assume $m \geq n$:

$$\lambda^{m+n} + \alpha_1\lambda^{m+n-2} + \ldots \alpha_n\lambda^{m-n} = 0 \quad (3.15)$$

It follows that

$$\lambda^{m-n}(\lambda^{2n} + \alpha_1\lambda^{2(n-1)} + \ldots \alpha_n) = 0$$

It is apparent that (a) there are $|m - n|$ eigenvalues $\lambda = 0$, (b) the rest of the eigenvalues, namely $2\min(m, n)$, appear in pairs $\pm\lambda$. The positive eigenvalues may represent bonding, the zero eigenvalues nonbonding, and the negative eigenvalues antibonding. We order the λ_i in a sequence of decreasing eigenvalues. When we now remember that the number of independent pairs is $\min(m, n)$, then the maximum bond order would be naturally the sum of all positive eigenvalues λ_i:

$$P_{AB} = \sum_{i=1}^{\min(m,n)} \lambda_i \quad (3.16)$$

This procedure would not allow for antibonding. It would also not be invariant under coordinate transformation. For instance, if in a local coordinate system on atom A the direction of the axis along the internuclear axis is inverted, the density matrix elements involving $p\sigma_A$ orbitals change sign and correspondingly some eigenvalues switch from $\pm\lambda$ to $\mp\lambda$. So a closer look at the eigenvectors, i.e., the hybrid pairs, is necessary. It seems appropriate to distinguish the hybrid pairs in three groups: (a) bonding if the overlap is larger than zero, (b) nonbonding if the overlap is zero, (c) antibonding if the overlap is less than zero. This is analogous to Mulliken's distinction of MOs in bonding, nonbonding, and antibonding.[10] It should be pointed out that the overlap has to be calculated after deorthogonalization of an OAO basis set. We now modify the definition of bond order by taking

$$P_{AB} = \sum_{i=1}^{\min(m,n)} \lambda_i \text{ sign } (S_{\overline{g}_i\overline{h}_i}) \quad (3.17)$$

where $\overline{g}_i$ and $\overline{h}_i$ are the deorthogonalized hybrid forms of g_i and h_i. This definition of P_{AB} is invariant under coordinate transformations, since the eigenvalues and eigenvectors of the density matrix are invariant under general rotations and translations of the coordinate system. So the total bond order is no longer necessarily a maximum (positive terms only) or a minimum (negative terms only), but may consist of both positive and negative terms. We call the situation of two atoms bonding if $P_{AB} > 0$, nonbonding for $P_{AB} = 0$, and antibonding for $P_{AB} < 0$.

Several remarks seem to be in order. It is not the aim of this method to attach a special meaning to each MO. In particular, the eigenvectors of the submatrices of the density matrix do not represent the MOs. So the purpose of this work is totally different from the maximum overlap concept[11,12] where the eigenvectors of the overlap matrix can represent under certain restrictive conditions, for instance, Hückel MOs. For practical purposes, it seems useful to transform the two-center density matrix of two atoms to a local coordinate system with axes along and perpendicular to the internuclear axis. This allows an analysis in σ and π contributions to the bond order and would seem to be more appealing to the experimental chemist. Here is also a chance to use a physical picture of the bond. If we deorthogonalize the hybrids, hybrid pairs can be plotted. They replace the classical σ- and π-bond pairs. In addition to those dominating ones, there appear corrections which had been previously ignored: those between nonadjacent bonds, lone pairs, etc.

IV. Applications

We have applied this concept of bond order to a large number of molecules using SINDO wave functions[13] which have proven their usefulness in several chemical reactions.[14-16] These wave functions suffice to demonstrate the qualitative aspects of our concept. Since comparisons had to be made on a consistent basis including full geometry optimizations, lack of available comparable ab initio data prevented an extensive ab initio analysis at this time.

In this section we present results of (a) bond orders for diatomics, (b) a bond order–bond length relation for CC, CO, and CH bonds, (c) a case of hydrogen bonding, (d) a case of bond breaking and bond forming during a chemical reaction.

In Table I bond orders of diatomics are collected in their ground state equilibrium with SINDO wave functions. Several facts are remarkable: (1) σ bond orders are not unity, but can deviate appreciably from one. (2) Hydride bonds are close to one in the range of 0.86–1.00. (3) Homonuclear diatomics have single bonds in H_2, Li_2, and F_2, a double bond in O_2, and a triple bond in N_2; CO is close to a triple bond. (4) B_2 appears as a double bond and C_2 as a triple bond. This latter result

Table I. Total Bond Orders of Diatomic Molecules in Their Equilibrium with σ Bond Orders in Parentheses

	H	Li	Be	B	C	N	O	F
H	1.0							
	(1.0)							
Li	0.93	1.0						
	(0.93)	(1.0)						
Be	0.86	1.33	0.0^a					
	(0.86)	(0.86)	(0.0)					
B	0.990	1.66	2.41	2.38				
	(0.990)	(0.82)	(0.93)	(1.38)				
C	0.998	1.91	2.77	2.43	3.45			
	(0.998)	(0.78)	(0.86)	(0.46)	(1.45)			
N	0.987	1.85	2.97	2.23	3.09	3.0		
	(0.987)	(0.85)	(1.22)	(1.02)	(1.13)	(1.0)		
O	0.97	1.96	3.08	1.84	2.76	2.41	2.0	
	(0.97)	(0.78)	(1.37)	(0.37)	(0.91)	(0.98)	(1.0)	
F	0.95	1.79	1.70	1.80	1.66	1.48	1.13	1.0
	(0.95)	(0.79)	(0.68)	(0.77)	(0.85)	(0.94)	(0.90)	(1.0)

^{a} Not bound.

Table II. A Comparison of σ Bonding in C_2 and N_2

	C₂				N₂			
			Two center parts of density matrix					
OAO	s_a	σ_a	s_b	σ_b	s_a	σ_a	s_b	σ_b
s_a	0	0	0.217	0.694	0	0	0.254	0.435
σ_a	0	0	0.694	−0.217	0	0	0.435	0.746
s_b	0.217	0.694	0	0	0.254	0.435	0	0
σ_b	0.694	−0.217	0	0	0.435	0.746	0	0
			Diagonalized density matrix					
	g_1+h_1	g_2+h_2	g_3+h_3	g_4+h_4	g_1+h_1	g_2+h_2	g_3+h_3	g_4+h_4
g_1+h_1	0.727				1.0			
g_2+h_2		0.727				0.0		
g_3+h_3			−0.727				0.0	
g_4+h_4				−0.727				−1.0

homonuclear diatomics with one occupied bonding MO the bond order stays one regardless of the basis set.

In Table III we list a few CC and CH bond orders in our and Mulliken's definition. It is clear from this table that Mulliken's definition is not compatible with the chemist's idea of single and multiple bonds. A particular problem arises in the case of cyclopropane, where even a localization procedure cannot determine the bond order uniquely (1.57 vs. 2.43). The reason is that the choice of the direction of the axes perpendicular to the internuclear axis is not unique and Mulliken's definition depends on this choice in cyclopropane. On first glance our definition is in agreement with popular notions of these bonds. For instance, the value of 1.32 in cyclopropane is explained by $0.88 + 0.32$ bent bond character plus 0.12 π bond character. In the sequence acetylene, ethylene, ethane, the ordering of bond orders might seem surprising at first. The bond energy of the CH bond decreases in the sequence just mentioned. But our definition is not based on a comparison of bond energies; rather it serves to characterize the valence multiplicity. A single bond in H_2 or Li_2 has the same bond order. If one wishes to reproduce bond energies, an empirical scheme such as the one

comes as most unexpected on the basis of the Aufbau principle according to which B_2 should be a single and C_2 a double bond. These bonds appear as pure π bonds with no σ bond present. It is apparent from the table that our result is based on a σ bond for both molecules. To understand this result better, we will compare the main features of C_2 and N_2 in terms of the density matrix in Table II. It appears that in the case of C_2 that $P_{s_a s_b} + P_{\sigma_a \sigma_b} = 0$ whereas it is 1 for N_2. Referring to (2.9) we see that the σ bonding in C_2 comes from the cross terms $P_{s_a \sigma_b}$ and $P_{\sigma_a s_b}$ whereas it comes from $P_{s_a s_b}$ and $P_{\sigma_a \sigma_b}$ in N_2. In the case of C_2 the SINDO MOs $2\sigma_g$ and $2\sigma_u$ have both a positive overlap charge, hence they are both bonding. In N_2 $2\sigma_g$ and $3\sigma_g$ have a positive overlap charge whereas $2\sigma_u$ has a negative overlap charge. When we know that ab initio results on N_2 by Scherr[17] get a negative overlap for $3\sigma_g$, we cannot attach too much significance to each single MO. We expect, however, that the sum of bond order contributions from all occupied MOs will not depend so strongly on the choice basis sets as net charges. It can be crucial only in Be_2, B_2, and C_2, when the overlap of the second σ MO changes sign. We shall investigate the basis set dependence in a subsequent paper. It frequently happens that the change of basis in terms of orbital exponents causes the increase of a coefficient on an atom in a normalized orbital and a decrease of another coefficient on another atom. In the case of net charges where $c_i{}^2$ is a determining contribution to the charge, there is no counterbalancing effect. But the bond order consisting of terms $c_{iA}c_{jB}$ can in principle counterbalance the increase of one factor by the decrease of the other; hence it is more stable under basis set changes. With respect to the integer bond orders, it is analytically not generally clear whether basis extensions affect these values. For

pursued extensively by Politzer[18] might be helpful. However, the name "bond order" seems confusing in this context when values of 1.55 for H_2 or 0.172 for Li_2 are obtained. Politzer's "bond orders" are really labels for bond strengths. For diatomics, Parr and collaborators[19] worked out an empirical bond charge concept. A comparison was made with simple bond orders and overlap populations in homonuclear diatomics. The model seems to work well except for bonds involving halogen atoms where the values are significantly larger than one. Later Simons and Parr[20] managed to show that in a

Table III. Various Bond Orders by This Method with Mulliken Numbers in Parentheses

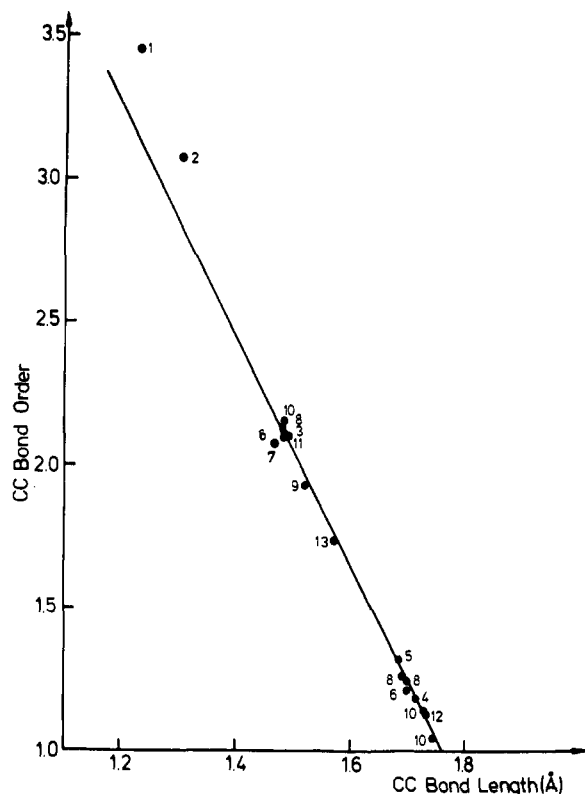|	Type of bond	
Molecule	XX′	XH
H_2		1.0 (1.0)
Li_2	1.0 (1.22)	
B_2	2.38 (2.33)	
C_2	3.45 (3.39)	
N_2	3.0 (3.87)	
NO	2.40 (3.10)	
O_2	2.0 (2.65)	
C_2H_2	3.07 (3.90)	0.966 (1.362)
C_2H_4	2.11 (3.10)	0.976 (1.356)
C_2H_6	1.20 (2.00)	0.988 (1.355)
CH_4		0.995 (1.357)
NH_3		0.990 (1.337)
H_2O		0.985 (1.299)
HF		0.954 (1.269)
Cyclopropane	1.32 (1.57)	0.977 (1.364)
	(2.43)	(1.368)

Figure 1. CC bond order in dependence of bond length: 1, C_2; 2, acetylene; 3, ethylene; 4, ethane; 5, cyclopropane; 6, propene; 7, allene; 8, cyclopentadiene; 9, ketene; 10, diketene; 11, 2,4-dimethylene-1,3-dioxetane; 12, cyclobutane-1,3-dione; 13, benzene.

Figure 2. CO bond orders in dependence of bond length: 1, CO; 2, ketene; 3, diketene; 4, CO_2; 5, formaldehyde; 6, 2,4-dimethylene-1,3-dioxetane; 7, cyclobutane-1,3-dione; 8, cyclobutane-1,2-dione.

multipole expansion their empirical model would yield bond charges that are maxima at equilibrium. After completion of this work, we became aware of a maximum overlap population postulate by Kaufman.[21] This attempt has met with different success.[22] It shares the difficulties and restrictions of the maximum overlap principle.[11] Coming back to the relative magnitudes of bond orders more generally in polyatomic molecules, we have compared bond orders and bond lengths for CC, CO, and CH. The results are presented in Figures 1–3. We find that we can correlate these two quantities linearly. For CC and CO bonds the bond orders decrease with increasing bond lengths. However, since the SINDO bond lengths appear too long by about 9%, a result to be expected from previous test calculations,[13] no quantitative recipe can be derived here. But we have tested the bond order–bond length relation also at the experimental geometries of the molecules considered and find a parallel shift toward smaller bond lengths with almost no change in slope of the correlation axis. Here we find also some support for the result of a triple bond in C_2. A triple bond fits in nicely with the fact that the bond length of C_2 is quite close to the CC bond in acetylene, which is undoubtedly a triple bond.

For CH bonds we obtain the result that the bond order increases with increasing bond length. This somewhat unexpected result can be explained on the basis of the covalent character of the MO LCAO bond order. Methane has more covalent bonding than acetylene. In this case the increasing bond order and also bond length corresponds to an increasing p character in the hybrid on C. Other investigators[23] have previously emphasized the decreasing s character with increasing bond length. From Figure 3 we see that the CH radical has the optimal covalent bond order. For larger distances as occur in hydrogen bonds we expect the bond order to decrease. Considering that a purely ionic bond would have bond
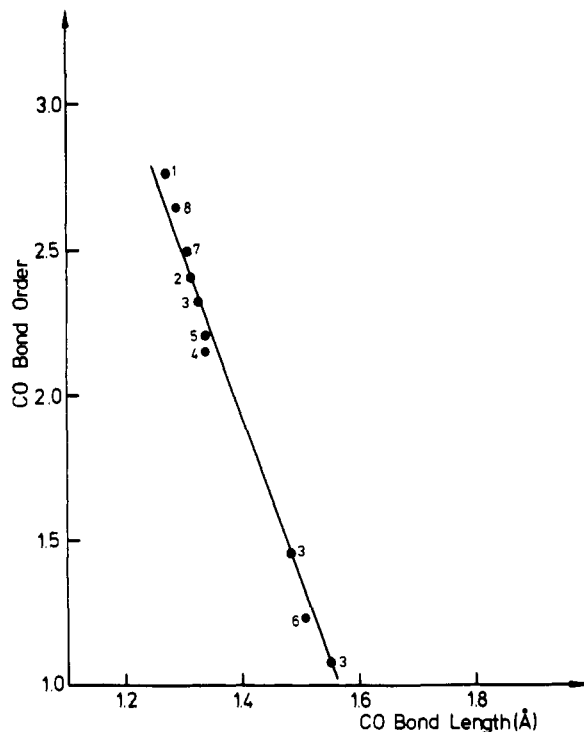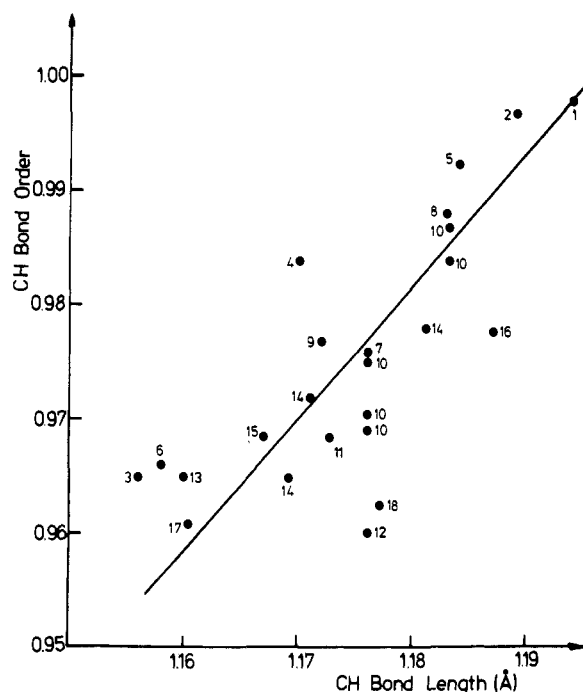

Figure 3. CH bond orders in dependence of bond length: 1, CH; 2, methylene singlet; 3, methylene triplet; 4, methyl; 5, methane; 6, acetylene; 7, ethylene; 8, ethane; 9, cyclopropane; 10, propene; 11, allene; 12, formaldehyde; 13, ketene; 14, diketene; 15, 2,4-dimethylene-1,3-dioxetane; 16, cyclobutane-1,3-dione; 17, HCN; 18, benzene.

order zero, we must introduce an additional ionic term to the total bond order.

$$P_{total} = P_{covalent} + P_{ionic}$$

We will not discuss this problem here, since such a term should depend on the atomic charges. Those are more crucially dependent on the choice of basis set and the charge definition.

In these figures there is no account of dominating antibonding effects as they might occur in non-nearest-neighbor bonds. In fact, the straight lines obtained if extended to larger distances do not describe bond orders for second or third neighbors. Antibonding occurs with second carbon–carbon neighbors in propene ($P = -0.14$) and allene ($P = -0.24$). For diketene small positive and negative bond orders occur for farther neighbors similar to results of Hückel calculations, e.g., in benzene. Such effects are introduced arbitrarily by a long-range factor by Cohen,[24] who uses the overlap population as a bond order concept. Cohen's work has the merit of emphasizing the necessity of rotational invariance. He uses a projection technique to achieve this. He gives also an appreciation of the literature. In contrast to Politzer[18] and Parr,[19] his halogen bond orders are rather small. His hydrocarbon bond orders are close to ours. We plan a detailed comparison in a subsequent paper.

We finally come to most interesting, but least explored fields where bond orders can be useful. First, we have tried to calculate bond orders for hydrogen-bonded system B_2H_6, with the following result: $P_{BB} = 0.988$, $P_{BH} = 0.974$, $P_{BH'} = 0.695$. BH is the normal, BH' the hydrogen bond. The geometry is basically correct ($R_{BB} = 1.95$ Å, $R_{BH} = 1.296$ Å, $R_{BH'} = 1.44$ Å, $\theta_{BBH'} = 47.4$) with the bond lengths too long by 10%. From here we expect that bond orders of hydrogen bonds are significantly reduced, their magnitude being about 0.7. Studies on other hydrogen-bonded systems will be undertaken. The BB bond order is less than that of a single bond (~ 1.20), but it is probably too large. We assess this as a shortcoming of the SINDO wave function. Indicative of this might be that the dissociation energy of B_2H_6 in two BH_3 is much too large in the SINDO method. We have also studied N_2O_4 with the result that $P_{NO} = 1.997$, practically the same as the bond order 2.002 in NO_2 and $P_{NN} = 0.23$. The latter bond order is the smallest we have found so far in any molecule in its equilibrium.

In nonequilibrium situations as they arise in chemical reactions the bond order can be a measure of whether a bond is broken or loosened. In a previous paper on the cyclopropane-propene isomerization[16] we have shown on the basis of bond order considerations that the reaction is concerted. Also the sequence of bond breaking and forming could be established. The consequence of these calculations can be experimentally tested inasmuch as they predict a hindered rotation of the methylene group during the CC bond opening. During the reaction, various bond orders change from bonding to antibonding and vice versa.

V. Conclusion

In this paper we presented the concept of a bond order to describe the valency multiplicity of bonds in molecules in their equilibrium and nonequilibrium situations. The method is applicable to all cases where a LCAO density matrix can be defined. In principle it can be used not only in closed-shell SCF but also in open-shell cases or with CI wave functions. The diagonalization of the two-center density matrix of a pair of atoms yields eigenvalues whose sum can be used to define a bond order. It is practical, but not necessary, to transform all the orbitals to a local coordinate system in which σ and π contributions to the bond order can be distinguished. After deorthogonalization the hybrid pairs can replace in a physical picture the classical σ and π bonds. Semiempirical calculations were performed to have a consistent basis for a variety of cases. They show qualitatively the general trend. The bond orders are basis set dependent, but less so than charges since changes in coefficients can often be counterbalanced. We are in the process of testing the results by ab initio calculations on a selected number of accessible systems.

References and Notes

(1) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, pp 101, 196.
(2) R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry", Interscience, New York, N.Y., 1959, p 27.
(3) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, pp 165–172.
(4) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y., 1966, pp. 134–141.
(5) C. A. Coulson, *Proc. R. Soc. London, Ser. A,* **169**, 419 (1939).
(6) B. H. Chirgwin and C. A. Coulson, *Proc. R. Soc. London, Ser. A,* **201**, 196 (1950).
(7) R. S. Mulliken, *J. Chem. Phys.,* **23**, 1833 (1955).
(8) P. O. Löwdin, *J. Chem. Phys.,* **18**, 365 (1950).
(9) R. S. Mulliken, *J. Chem. Phys.,* **23**, 1841 (1955).
(10) R. S. Mulliken, *J. Chem. Phys.,* **23**, 2338 (1955).
(11) P. G. Lykos and H. N. Schmeising, *J. Chem. Phys.,* **35**, 288 (1961).
(12) R. Bartlett and Y. Öhrn, *Theor. Chim. Acta,* **21**, 215 (1971).
(13) P. Coffey and K. Jug, *J. Am. Chem. Soc.,* **95**, 7575 (1973).
(14) P. Coffey and K. Jug, *Theor. Chim. Acta,* **34**, 213 (1974).
(15) K. Jug and J. Chickos, *Theor. Chim. Acta,* **40**, 207 (1975).
(16) K. Jug, *Theor. Chim. Acta,* **42**, 303 (1976).
(17) C. W. Scherr, *J. Chem. Phys.,* **23**, 569 (1955).
(18) P. Politzer, *J. Phys. Chem.,* **80**, 283 (1976); *J. Chem. Phys.,* **51**, 459 (1970); **50**, 2780 (1969).
(19) F. Borkmann, G. Simons, and R. G. Parr, *J. Chem. Phys.,* **50**, 58 (1969).
(20) G. Simons and R. G. Parr, *J. Chem. Phys.,* **55**, 4197 (1971).
(21) J. J. Kaufman, *Int. J. Quantum Chem.,* **1S**, 485 (1967).
(22) J. J. Kaufman and L. M. Sachs, *J. Chem. Phys.,* **52**, 638 (1970); R. Manne, *Int. J. Quantum Chem.,* **2**, 68 (1968).
(23) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron,* **11**, 96 (1960).
(24) I. Cohen, *J. Chem. Phys.,* **57**, 5077 (1972).