Bond Order as a Tool for Molecular Structure and Reactivity

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The concept of bond order can be derived exclusively from the properties of the density matrix. After definition of a density operator in the basis of a self-consistent-field (SCF) or configuration interaction (CI) wavefunction which is built from molecular orbitals (MO's), the MO's are expanded in orthogonalized atomic orbitals (OAO's) and the density matrix is constructed over OAO's. The density matrix is partitioned in diatomic parts, for which the eigenvalues are determined. The sum of positive eigenvalues weighted with appropriate weighting factors, which are derived with a projection technique, constitutes the bond orders between atomic pairs. In a variety of applications to ground and excited state equilibria and reactions the usefulness of this property is demonstrated. Special attention is focussed on aromatic systems which can be classified with this property.

1. INTRODUCTION

Bond order is the expression for the valence multiplicity of pairs of atoms in molecules. The valence bond (VB) method is the outgrowth of the chemists' expectation that atoms are bound in molecules by electron pairs. On its lowest level of approximation, this localized description is most appropriate for localized σ bonds, which are thought of as linear combinations of s orbitals or directed hybrids sp, sp^2 or sp^3 on the two bonding centers. π bonds in conjugated and aromatic molecules need a delocalized description for which the molecular orbital (MO) method offers the suitable approach. In the latter method there is no natural way to measure the extent of electron pairing in the molecular bonds. Since the early calculations of molecules had to be restricted to the energetically highest lying valence electrons, the treatment of π electrons in conjugated systems became more and more popular. For such systems Coulson[1] defined the bond order between two atoms in the MO method in its linear combination of atomic orbital (LCAO) form as

$$P_{\mu\nu} = \sum_{i}^{\text{occ}} n_i c_{i\mu} c_{i\nu} \tag{1.1}$$

with

$$\psi_i = \sum_{\mu} c_{i\mu} \lambda_{\mu}$$

μ, ν are AO's and i occupied MO's with occupation number n_i. The formula assumed orthogonal atomic orbitals (AO's) λ with one orbital per atom. Hückel's π electron method with its neglect of overlap offered the most useful basis for application. Later Chirgwin and Coulson[2] extended the formalism to non-orthogonal AO's χ with overlap $S_{\mu\nu}$ different from zero

$$P_{\mu\nu} = \frac{1}{2} \sum_i^{occ} n_i \left(c_{i\mu} \sum_\rho S_{\nu\rho} c_{i\rho} + c_{i\nu} \sum_\rho S_{\mu\rho} c_{i\rho} \right) \tag{1.2}$$

Mulliken[3] removed the restriction to one orbital per atom. His expression for orthogonalized AO's is

$$P_{AB} = \sum_i^{occ} n_i \sum_\mu^A \sum_\nu^B c_{i\mu} c_{i\nu} \tag{1.3}$$

This expression suffers from two defects: a) It is not invariant under coordinate transformation, b) it yields bond orders which are not in line with standard expectations, e. g. CC bond orders are approximately 2 in ethane, 3 in ethylene and 4 in acetylene.

Mulliken's expression for nonorthogonal orbitals

$$P_{AB} = \sum_i^{occ} n_i \sum_\mu^A \sum_\nu^B (1 + S_{\mu\nu}) c_{i\mu} c_{i\nu} \tag{1.4}$$

is arbitrary and suffers the same defects as (1.3). Much confusion was created in later years by papers which referred to bond orders, bond indices or bond overlap but mean a property different from valence multiplicity. In this category we can include a) the bond quantities and bond characteristics of Ruedenberg[4] which use weighting factors in (1.4) different from $1 + S_{\mu\nu}$, b) the bond index of Wiberg[5], which is really a valence number since it is always positive and cannot describe antibonding situations, c) the bond orders by Parr and Borkmann[6] which are really bond charges, d) the modified bond orders by Politzer[7] which reflect bond strength, e) the bond overlap by Kaufmann[8] which is a charge distribution. Much of this confusion was overcome by Cohen[9] who reviewed the literature and suggested a modification of Mulliken's form (1.4)

$$P_{AB} = \sum_\mu^A \sum_\nu^B P_{\mu\nu} (S_{\mu\nu} + f_{\mu\nu} g_{\mu\nu}) \tag{1.5}$$

with

$$P_{\mu\nu} = \sum_i^{occ} n_i c_{i\mu} c_{i\nu}$$

$f_{\mu\nu}$ is a long range factor and $g_{\mu\nu}$ is an atomic hybridization and nonorthogonality factor. Although Cohen's numbers are close to our expectations, the method has the drawback of arbitrariness from the start, e. g. Eq. (1.4), and the introduction of factors f and g. To its assets we can count the invariance with respect to coordinate transformations.

To remove this arbitrariness we suggested a maximum bond order principle[19] which relied exclusively on the information provided by the density matrix $P_{\mu\nu}$ of Eq. (1.1). In the following sections we shall describe the method,

its modifications and applications to ground and excited state equilibria and reactions.

2. METHOD

We consider a CI wavefunction of a molecule with N eletcrons

$$\Psi = \sum_I A_I \Psi_I \qquad (2.1)$$

consisting of configurations Ψ_I which are built from MO's ψ_i

$$\Psi_I = | \psi_{i_1} \ \psi_{i_2} \ldots \psi_{i_N} | \qquad (2.2)$$

$$I = \{ i_1 < i_2 \ldots < i_N \}$$

The density operator is the projection operator of Ψ^{11}

$$P_{op} = | \Psi > < \Psi | = \sum_{I,J} A_I A_J | \Psi_I > < \Psi_J | = \sum_{I,J} A_I A_J \sum \varrho_{IJij} | \psi_i > < \psi_j | \qquad (2.3)$$

with

$$\varrho_{IJij} = \begin{cases} (-1)^{s-t} \{ I - i \} = \{ J - j \}, \ i = i_s, \ j = j_t \\ 0 \end{cases}$$

We then obtain

$$P_{op} = \sum_I A_I^2 \sum_{i_I} | \psi_{i_I} > < \psi_{i_I} | + \sum_{\substack{I,J \\ I \neq J}} A_I A_J (-1)^{s-t} | \psi i_{sI} > < \psi j_{tJ} | \qquad (2.4)$$

We define now the density matrix $P_{\mu\nu}$ over atomic orbitals in line with (1.1) and (2.4) as

$$P_{\mu\nu} = < \mu | P_{op} | \nu > = \sum_I A_I^2 \sum_{i_I} c_{i_I\mu} c_{i_I\nu} + \sum_{\substack{I,J \\ I \neq J}} A_I A_J (-1)^{s-t} c_{i_{sI}\mu} c_{j_{tJ}\nu} \qquad (2.5)$$

In the following we shall refer to orthogonalized AO's which are Schmidt orthogonalized on each atom and subsequently Löwdin orthogonalizied between different atoms[12]. The density matrix (2.5) can be subdivided in blocks referring to atoms A, B, C . . . in the molecule

$$P_{\mu\nu} = \begin{pmatrix} P^{AA} \ P^{AB} \ P^{AC} \ \cdots \\ P^{BA} \ P^{BB} \ P^{BC} \\ P^{CA} \ P^{CB} \ P^{CC} \\ \cdots \end{pmatrix} \qquad (2.6)$$

Intraatomic blocks P^{AA}, P^{BB}, P^{CC} . . . refer to charge and hybridization on each atom, P^{AB}, P^{AC}, P^{BC} . . . refer to the bonding between atomic pairs. The idea is now to select diatomic portions of the density matrix

$$P_{\mu\nu}^{AB} = \begin{pmatrix} 0 & P^{BA} \\ P^{AB} & 0 \end{pmatrix} \qquad (2.7)$$

which are related to the bonding of atomic pair A, B. The characteristics of this matrix are its eigenvalues. From the symmetry properties of this matrix it can be shown that the eigenvalues λ_i occur in pairs $\pm \lambda_1$, $\pm \lambda_2$ . . . .[10] If the number of AO's on atom A is n_A and on atom B is n_B, $| n_A - n_B |$ eigenvalues

must vanish. The pairing property can be better understood if one considers that the trace of $P_{\mu\nu}^{AB}$ in (2.7) is zero and that this trace is invariant under a unitary transformation of the basis set. This unitary transformation yields a set of $n_A + n_B$ linear combinations of OAO's on A and B. We call these combinations bond order orbitals and their eigenvalues bond order eigenvalues. Because of the symmetry of matrix (2.7) and the pairing property of the bond order eigenvalues, it is clear that the bond order orbitals also occur in pairs, namely bonding and antibonding pairs. For different n_A and n_B, there are also $|n_A - n_B|$ nonbonding bond order orbitals.

It is now essential to realize that the bond order P^{AB} between atoms A and B cannot be the sum of all eigenvalues of (2.7) since this would be zero, but that it must be the sum of all positive eigenvalues only. In this simple form, the bond order obeys the variation principle in a similar fashion as the energy of an effective hamiltonian operator which generates the MO's. We select the MO's according to a minimum principle for the energy and distribute the electrons starting from the lowest eigenvalue. The bond order is obtained by a maximum principle and the number of bond order eigenvalues selected is given by the pairing number. This number is the minimum of orbitals n_A and n_B. For instance, in a minimal basis set with a $1s$ orbital on hydrogen, this orbital can form only one bonding pair and one antibonding pair, regardless of how many orbitals are centered on the second atom. So only one eigenvalue can be characteristic for the bonding of H to another atom.

It is now important to point out that the positive bond order eigenvalues do not always belong to *bonding* bond order orbitals. Since we are dealing with OAO's which have no overlap, Mulliken's overlap criterion of bonding and antibonding[13] is not appropriate. Instead we shall use a projection criterion[14]. The basis OAO's on atoms A and B are considered as vectors in Hilbert space. Each hybrid on both atoms, which is portion of a bond order orbital, is a linear combination of the basis vectors and has a certain direction in this vector space. If one spans the whole vector space by a basis common to both atoms, the projection of the unit vectors for the two hybrids which form the bond order orbital is the weighting factor for the bond order eigenvalue. Bonding orbitals have parallel, antibonding orbitals antiparallel components. Initially[10] we had deorthogonalized the OAO's in the bond order orbitals and applied Mulliken's overlap criterion to determine the weighting factors $+1$ for bonding and -1 for antibonding. This procedure leads to discontinuities in the bond order[13].

3. GROUND STATE EQUILIBRIA

3.1. *Bond Order Orbitals and Eigenvalues*

To clarify the details of covalent bonding between atomic pairs, it would be appropriate to start from the bond order orbitals. In first-row calculations the semiempirical MO method SINDO1[15] has demonstrated reliability in binding energy and geometry[16] and will be used in the following applications. Table I lists weighted bond order eigenvalues for molecules containing C, N and O atoms. The weighting factors are obtained by the projection criterion[14]. The sum of all weighted bond order eigenvalues is the total bond order between a pair of atoms. In a minimal basis set with valence orbitals only, there are four atomic orbitals s, px, py, pz for first-row elements. The diagonalization of the diatomic part (2.7) of the density matrix for first-row atoms yields eight

bond order orbitals which are linear combinations of the eight AO's. Four of them belong to positive eigenvalues. In a local coordinate system two of these are σ orbitals called 1σ and 2σ and two are π orbitals called $1\pi_x$ and $1\pi_y$ in the Table. The weighting factor is positive for the bonding, zero for the nonbonding and negative for the antibonding orbitals. If the local distinction betwen σ and π is not maintained in the global molecular coordinate system, then σ and π orbitals are mixed. We indicate this by an asterisk.

TABLE I

Weighted Bond Order Eigenvalues for Molecules Containing C, N and O Atoms

Molecule	Bond	Total bond order	1σ	Bond order orbital 2σ	$1\pi_x$	$1\pi_y$
C_2H_2	CC	2.931	0.992	—0.061	1.000	1.000
C_2H_4		2.155	1.000	—0.036	1.000	0.192
t-C_4H_6		2.106	0.996*	—0.043	0.969*	0.184*
$C_4H_4(D_{2h})$		2.039	0.992*	—0.093*	1.000	0.141*
C_6H_6		1.750	0.985	—0.041	0.667	0.143
t-C_4H_6		1.295	0.978*	—0.038*	0.245	0.110*
C_3H_6		1.260	0.968*	—0.014*	0.129	0.196*
C_2H_6		1.254	1.000	—0.018	0.137	0.137
(1.1.1)propellane**		1.147	0.678(p)	0.191(s)	0.139	0.139
(1.1.2)propellane**		1.091	0.754*	0.204*	0.136	—0.004*
(1.2.2)propellane**		1.073	0.894*	0.182*	0.022	—0.025*
$C_4H_4(D_{2h})$		0.980	0.965*	—0.058*	0	0.072*
HCN	CN	2.851	0.924	—0.069	0.998	0.998
HNC		2.616	0.839	—0.109	0.944	0.944
$HCONH_2$		1.296	0.941*	—0.045	0.274*	0.127*
CO	CO	2.773	0.951	0	0.911	0.911
CO_2		2.186	0.908	—0.060	0.668	0.668
H_2CO		2.250	0.961	—0.031	0.982	0.338
CH_3OH		1.290	0.971*	—0.022*	0.185*	0.157*
N_2	NN	3.000	1.000	0	1.000	1.000
N_2H_2		2.230	0.996*	0.011*	1.000	0.225*
N_2H_4		1.207	0.991*	—0.008*	0.120*	0.104*
NO	NO	2.421	0.990	0.000	0.964	0.468
NO_2		1.968	0.908*	0.047*	0.694	0.414*
F_3NO		1.393	0.786	—0.084	0.345	0.345
H_3NO		1.022	0.755	—0.077	0.172	0.172
O_2	OO	2.000	1.000	0.000	0.500	0.500
O_3		1.708	0.929*	0*	0.704	0.075*
H_2O_2		1.163	0.996*	0.000	0.094*	0.073*

* σ and π mixing   ** central bond

A detailed inspection of the table yields the following general result. There is one dominant σ bonding orbital with an eigenvalue mostly close to 1. We refer to this orbital as the standard σ bond. In addition, we have a small and usually antibonding contribution to the σ bonding. This contribution can be ascribed to the nonbonding or antibonding portion of the MO's. In π electron systems there is a dominant π contribution, but perpendicular to this bond there is also π bonding. In linear systems this bonding equals the other π part. In planar systems it is usually much smaller and accounts for the in-plane π bonding. Polarization reduces the main components of σ and π bonding and decreases the value below the standard of unity. The additional two small σ

and π contributions which are usually neglected in a localized valence bond description modify the main part. So the bond order of ethane is 1.254 and of ethylene 2.155 due to small π contributions which are usually ignored. Of particular interest are unusual systems as the propellanes where we have analysized the central bond. The strongest bond in the sequence is in the smallest (1.1.1)propellane, a conclusion which is in agreement with experimental results[17]. The magnitude of the total bond order is determined in this sequence by the π contributions which make the (1.1.1)propellane central bond the strongest. The dominant σ contribution is here particularly small and is mainly composed by $p\sigma$ bonding of the highest occupied molecular orbital (HOMO). This is understandable since there are three other »normal« CC bonds in the half space in addition to the unusual central bond. Another set of unusual molecules is F_3NO and H_3NO. The NO bond order of F_3NO is much stronger than that of H_3NO due to π bonding. As a consequence the NO bond in F_3NO is shorter than in H_3NO, also in agreement with experiment[18].

Table II lists weighted bond order eigenvalues for molecules containing F, B, Be and Li atoms. The situation here is in principal similar to that in Table I. However, stronger polarization can reduce the main values substantially particularly in polar bonds involving Li atoms. Interesting here is the bonding in BF_3 and B_2H_6 where the empty p orbitals of boron are used. In the first case the lone pairs of F yield a »back donation« effect for the σ electrons increase of the charge on F. In the second case the BB π bond stems mainly from the binding of the two perpendicular hydrogens. We have listed also a number of unusual Li compounds which were recently discussed by Schleyer[19]. There is substantial π bonding in the CLi bond of CLi_4, CLi_6 OLi_4^{2+} and OLi_4. CLi_6 and OLi_4 are definitely unusual in their coordination number. They have

TABLE II

Weighted Bond Order Eigenvalues for Molecules Containing F, B, Be, Li Atoms

Molecule	Bond	Total bond order	1σ	Bond order orbital 2σ	$1\pi_x$	$1\pi_y$
B_2F_4	BF	1.461	0.881*	—0.026*	0.441	0.165*
BF_3		1.404	0.850	—0.030	0.384	0.201
BF		1.872	0.845	0	0.513	0.513
B_2H_6	BB	1.047	0.566	—0.018	0.402	0.097
B_2F_4		1.096	0.980*	—0.025*	0.071	0.071
BeC	BeC	1.070	0.425	—0.240	0.885	0
BeF_2	BeF	1.550	0.779	—0.058	0.414	0.414
LiC	LiC	0.760	0.806	—0.253	0.206	0
C_2Li_2		0.900	0.592*	—0.002*	0.315	—0.005*
$H_2C=CLi_2$		1.225	0.821*	—0.008*	0.243	0.168*
CLi_4		1.487	0.728	—0.109	0.434	0.434
CLi_6		0.942	0.551	—0.269	0.331	0.331
OLi_4^{2+}		1.149	0.572	—0.041	0.309	0.309
OLi_4		1.036	0.551	—0.211	0.349	0.349
$H_2C=CLi_2$	LiLi	0.058	0.038*	—0.005*	0.087	—0.061
CLi_4		0.312	0.289*	—0.165*	0.168	0.020*
CLi_6		0.545	0.338*	0.142*	0.105	—0.091*
OLi_4^{2+}		0.152	0.121*	0.003*	0.055	—0.029*
OLi_4		0.643	0.489*	0.113*	0.074	—0.033*

* σ and π mixing

substantially reduced σ bonds. This can be explained because the fifth valence electron pair is causing an antibonding effect in the CLi bond. But even CLi_4 and OLi_4^{2+} are not the usual molecules which their coordination number might suggest. They show also reduced σ bonding. Here we might still prefer to ascribe this to polarization. Looking at the LiLi bonding we find that the CLi bond order decrease from CLi_4 to CLi_6 and OLi_4^{2+} to OLi_4 is accompained by an LiLi bond order increase which is due to σ bonding. So the addition of further Li atoms increases the »metallic« cluster bonding and decreases the covalent central bonding. This conclusion is in agreement with Schleyer's.

We do not present figures of the bond order orbitals themselves, but refer to previous work.[20,21]

3.2. Bond Order and Bond Length

In addition to the purely theoretical information provided in the previous paragraph, bond orders can be related to experimental quantities. For π electron systems there was a correlation between bond order and bond length. In the all valence electron method SINDO1 a similar correspondence can be deduced. Since earlier work on this subject[10,21] was based on the original SINDO[22] which resulted in 10⁰/₀ errors in the bond lengths, we present the results in the much more accurate SINDO1 framework for CC, CO and CH bonds. Figures 1 and 2 show a roughly linear dependence of bond order and bond
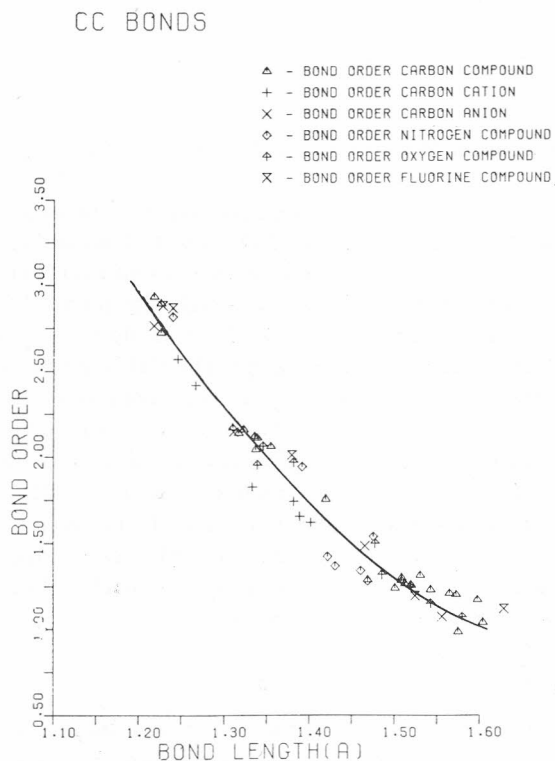

Figure 1. Correlation of Bond Order with Bond Length (Å) for CC Bonds.
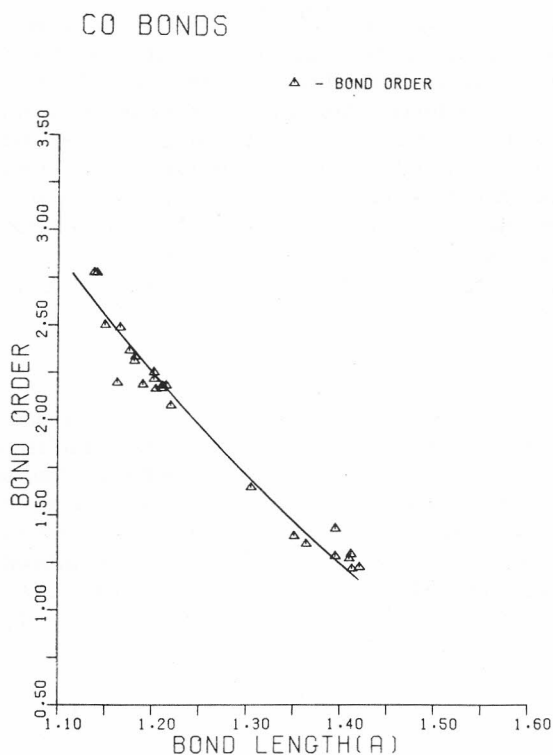
CO BONDS

△ - BOND ORDER

Figure 2. Correlation of Bond Order with Bond Length (Å) for CO Bonds.

length. Increasing bond length is accompained by decreasing bond order. Diagrams of this sort can be given for NO, NN, CN bonds *etc.* This effect is due to a decrease in π bonding. For CH bonds no similar dependence can be derived. In Figure 3 we have fit a curve through the points to emphasize that there are two opposing effects. The first effect is due to polarization of CH bonds and is found at small CH bond lengths. The CH bond in acetylene is more polarized than in ethylene, which in turn is more polarized than in ethane. So the covalent bond order increases linearly with increasing bond length in this sequence. The second effect is due to dissociation and is found at large bond lengths. Cases of this sort occur in unusual ions, *e. g.* CH_5^+ with weak CH bonds. The covalent bond order must decrease if the bond is broken. So a linear decrease of bond order with bond length seems appropriate as the simplest approximation. Since both effects oppose each other no simple correlation is possible for medium CH distances.

3.3. *Bond Order and Search for Equilibria*

The previous relation between bond order and bond lengths is valid in the presented form only for equilibrium geometries. Deviations from equilibrium bond length are not necessarily accompanied by a change in bond order.

CH BONDS

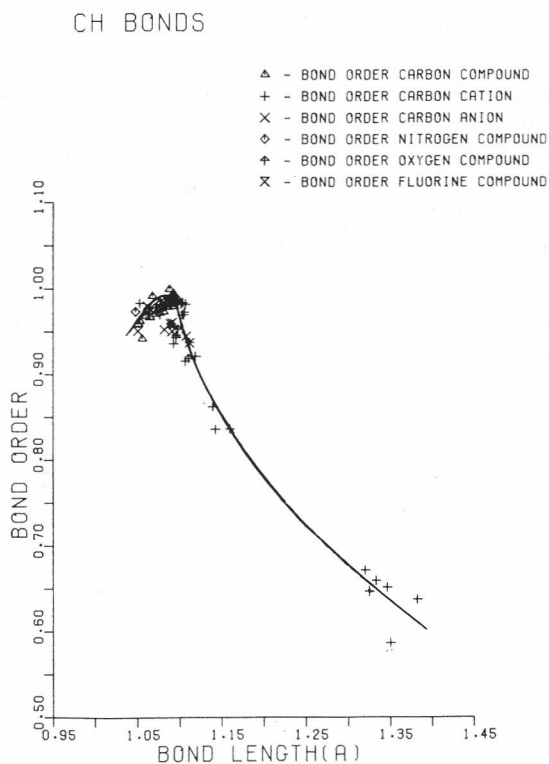Figure 3. Correlation of Bond Order with Bond Length (Å) for CH Bonds.

In an SCF calculation of ethylene the bond order is about 2 regardless of substantial lengthening or shortening of the CC bond. This property can aid us in finding equilibrium geometries. We can improve the bond length of an initial calculation not only by looking at the energy gradient, but alternatively at the initial bond orders. In this fashion one might be able to extrapolate in an iterative scheme, involving bond order and bond length, equilibrium bond lengths. A second and equally important property of bond order is its reflexion of the inherent symmetry of the nearest equilibrium. If we start with a regular pentagon for the $C_5H_5^+$ ring system because we expect that the bond lengths are equal in its singlet equilibrium, the bond orders will tell us immediately that this assumption is wrong. From the bond orders we find localized bonding with unequal bond orders even for equal bond lengths. In the subsequent optimization the bond order guides us to the correct antiaromatic localized structure.

On the other hand, if we start with a lower symmetry than the actual symmetry of the equilibrium, the bond orders of the important bonds are much closer and guide us towards equal bond lengths. Considerations of this sort have helped us to find the D_{3h} and D_{4h} equilibria of OLi_6, a system for which the »natural« structure would be O_h symmetry. The latter does not exist as equilibrium on the energy hypersurface.

3.4. *Bond Order and Bond Angles*

Bond orders can be directly related only to bond lengths. If we include the nonbonding bond distances in this relationship we can replace bond angles by bond lengths. However, the relation is no longer linear as in Figures 1 and 2. Some qualitative results are presented in Table III. Here we have related bond orders with large CC and OO bond distances and their corresponding bond angles. It is gratifying to see that the increase of antibonding is accompained by an increase in bond angle. The quantitative aspect for the search of equilibria mentioned in 3.3 has not been explored for bond angles and from this table it seems a difficult problem, if the nature of the outer atoms is not taken into account. So rather than bond angles, the bond lengths offer a clue for nonbonding distances, if the approximately linear relationship of Figures 1 and 2 is modified and extended to such situations.

TABLE III

Correlation of Bond Order with Bond Angles and Nonbonding Bond Distances

Molecule	Bond	Bond order	Bond angle degree	Bond length A°
O_3	OO	—0.63	122.1	2.171
NO_2		—0.76	137.9	2.236
CO_2		—0.82	180	2.380
$C_3H_5^+$	CC	0.48	124.6	2.449
C_3H_5		0.02	128.9	2.526
$C_3H_5^-$		—0.40	134.7	2.571

3.5. *Bond Order and Basis Sets*

Little work has been done on the basis set dependence of bond orders. This is due mainly to the difficulty in defining projection factors for arbitrary AO basis sets and the inconvenience of the *ab initio* programs which use nonorthogonal AO's instead of the orthogonalized needed here. Only the two systems C_2 and N_2 were investigated[23]. The question in C_2 was: Is there σ bonding in this molecule? Due to the lack of the necessary degrees of freedom in minimal basis set calculations, the bond order is always zero regardless of whether *ab initio* or semiempirical wavefunctions are used. Double and triple zeta *ab initio* calculations show that there is σ bonding amounting to a bond order of about 0.6. The question in N_2 was: Is the bond order invariant with increase of basis set? We found the values of 3 for all cases considered. We expect from the two crucial cases that the bond order is a fairly stable property much more than net charges are.

4. GROUND STATE REACTIONS

Ground state reactions are accompanied by distortions of equilibria involving bond lengths, bond angles and dihedral angles. The dependence of small changes in equilibrium bond lengths and bond angles and the twist around single and double bonds was investigated previously.[24,21] No maximum of the CC bond order was found at the equilibrium geometry contrary to the expectations of overlap criteria.[8,25] The CH bond order showed a minimum at equi-

librium. The effect of changes in the CCH angle on CC and CH bond orders
was quite small and showed no simple trend. So these bond orders are not
helpful in determining bond angles. Much more interesting is the change of
bond order with rotation about single bonds and double bonds. We found a
correspondence of maximizing the central bond order in C_2H_6 and H_2O_2 and
minimizing the outer bond orders with energy minimization. Equally inter-
esting is the effect in ethylene where again a maximization of bond order is
accompanied by a minimization of energy. However, orthogonal ethylene has
not a bond order of one, but substantially higher due to hyperconjugation.[21]
The latter calculation is based on configuration interaction, since the rotation
barrier in ethylene can be reasonably obtained only in this way.

So far we have considered only distortions which end up in the equilibrium
of the reactant. However typical chemical reactions lead from reactants to
different products. Among them are isomerization, addition, elimination and
substitution reactions. They all involve transition states. Two possibilities exist:
1) A product is reached by passing through a sequence of transition states
along one reaction pathway, 2) a product can be reached alternatively through
different pathways each with at least one transition state. If at least two transit-
ion states are involved in one pathway, an intermediate exists. Transition
states and intermediates are extrema on the hypersurface. Their geometrical
structure is often so unusual that it cannot be related to standard ideas of
bonding. Here bond orders can be particularly helpful. The bond orders tell
us how much bond breaking and bond forming has proceeded during the
reaction.

We found in the cyclopropane-propene isomerization[26] at the transition state
that the breaking and forming of the CH bond for the migrating hydrogen is
simultaneous and that most of it occurs before the transition state is reached.
The ring opening occurs somewhat later with the related CC bond loosening
but no increase in the double bond character of the adjacent CC bond before
the transition state is reached from the cyclopropane side. The final ring bond
breaking and CH migration as well as the increase of the CC double bond cha-
racter occur only after the transition state. Bond orders are indicative in
fragmentation reactions for the site of bond breaking. The diketene fragment-
ation and isomerization was studied in this fashion.[27] The weakest ring bonds
were involved in the reaction along the most favorable reaction pathway.
It might be quite interesting to follow the change of bond order upon sub-
stitution and see the change in activation energy.

5. EXCITED STATES

π electron bond orders for the prediction of excited state equilibria were
suggested by Julg[28] and later extensively advanced by Nakajima[29]. A linear
relationship between π bond order and bond length is assumed not only for
ground state equilibria but also used for excited state equilibria. This procedure
is justifiable only in the following context: 1) We know that the π electrons in
a π electron method simulate the behaviour of all valence electrons.

This means the charges calculated in π electron systems reflect the overall
effect of all electrons rather than the π electrons. In heteropolar bonds the σ
electrons are polarized toward the more electronegative atom, whereas the
π electrons try to reduce the developing potential difference by an opposite

»flow«. Since the σ effect usually dominates, a π electron method gives the right total charge for the wrong reasons. 2) π electron methods cannot describe deviations from planarity in π electron systems and their application is restricted to the assumption that the excited states are still planar. We have shown in several papers[30-32] that nonplanarity of excited states of π electron systems is quite common. The mixing of σ and π requires a treatment of bond orders which is based on all valence electrons.

If we go beyond the equilibria to photochemical reactions the use of an all-valence electron bond order is imperative. In an investigation of the cyclopentanone reaction[33] the breaking and forming of bonds can be followed conveniently with our bond orders in the excited states in the same way as we do this in the ground state. Here the density matrix must be defined with a CI wavefunction.

6. AROMATICITY

We have recently advanced the idea that the ring current in a ring system, which is one of the criteria used to define aromaticity, can be related to the weakest bond in the ring[34]. This weakest bond characterized by its bond order offers the greatest resistance to a ring current. Consequently it determines the magnitude of the ring current. This concept was used to classify more than seventy monocyclic and polycyclic compounds. Agreement between this concept of aromaticity and the resonance energy concept[35-37] was usually good in monocyclic compounds except for C_3O_3 for which the resonance energy method predicted aromaticity[36] contrary to all expectations. Our ring current concept classifies it as antiaromatic. We find this molecule unstable with respect to fragmentation in 3 CO using the SINDO1 method.[15] Differences in polycyclic compounds between the two concepts occur for cases with weak inner bonds. These bonds do not influence an outer ring current but determine the stability of the molecule as a whole.

Since we connect aromaticity with states of molecules no sign of it should show up in UV spectra. We can classify the excited states of aromatic systems with the same criterion. As a general observation it was found that the aromaticity of aromatic rings is reduced upon excitation.[29-31] This is due to replacement of bonding orbitals by antibonding orbitals which in turn reduces the bond orders. We conclude that the reactivity of excited states of aromatic rings is greatly changed compared to the ground states. We are presently engaged in the task of investigating the increase of aromaticity in the excited states of systems which are antiaromatic in the ground state. This would open new routes for the synthesis of antiaromatic systems.

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SAŽETAK

Red veze kao pribor za proučavanje molekulskih struktura i reaktivnosti

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Red veze može se odrediti direktno iz svojstava matrice gustoće. U tu se svrhu najprije definira operator gustoće u bazi SCF ili SCF-CI valnih funkcija, koje su izgrađene od molekulskih orbitala na poznati način. Ove posljednje mogu se smatrati linearnim kombinacijama ortogonalnih atomskih orbitala (OAO). To znači da se matrica gustoće može konstruirati preko OAO. Nadalje, matricu gustoće možemo razbiti na dvoatomske dijelove čije se vlastite vrijednosti mogu lako odrediti. Zbroj pozitivnih vlastitih vrijednosti pomnoženih s odgovarajućim težinskim faktorima daje redove veza između parova atoma. Pokazano je da su tako dobiveni redovi veza vrlo korisni za diskusiju o svojstvima osnovnoga i pobuđenih stanja, kemijske reaktivnosti pa čak i aromatičnosti kojoj je poklonjena posebna pažnja.