

Bond Order Orbitals and Eigenvalues

Karl Jug

Contribution from Theoretische Chemie, Technische Universität Hannover, Hannover, West Germany. Received October 4, 1977

Abstract: A previously proposed bond order principle is illustrated by analysis of its components. Semiempirical CC bond order orbitals are presented for a few characteristic cases, including an extension for CI calculations. The corresponding eigenvalues are tabulated for CC, CN, CO, NN, NO, and OO bonds of a large number of selected molecules.

I. Introduction

In a previous paper¹ we suggested a maximum bond order principle helpful in dealing with fractional σ and π bonds. It was based on the diagonalization of the two-center parts of the corresponding density matrix of each pair of two atoms in a molecule. The principle was capable of distinguishing between bonding, nonbonding, and antibonding situations. The bond order between two atoms A and B could be written as a sum of eigenvalues of the corresponding density matrix parts multiplied by the sign of the overlap of the corresponding hybrids \bar{g}_i on A and \bar{h}_i on B:

$$P_{AB} = \sum_i^{\min(m_A, n_B)} \lambda_i \text{sign}(S_{\bar{g}_i \bar{h}_i}) \quad (1.1)$$

Here λ_i are the positive eigenvalues of the two-center density matrix parts referring to A and B only. The underlying basis set was assumed as Schmidt orthogonalized on each atom and subsequently symmetrically orthogonalized. Diagonalization of the two-center parts of the density matrix yields two-center bond order orbitals $b_i = g_i + h_i$ over symmetrically orthogonalized AOs. After deorthogonalization we obtain the bond order orbitals $b_i = \bar{g}_i + \bar{h}_i$ over the usual AOs. The overlap S between \bar{g}_i and \bar{h}_i is calculated to determine whether b_i is bonding, nonbonding, or antibonding. Positive overlap means bonding, zero overlap nonbonding, and negative overlap antibonding.² Finally the sum is taken over the minimum number of basis orbitals m_A and n_B on both atoms considered. We previously proved that the eigenvalues occur in pairs $\pm\lambda_i$ of positive and negative values and that $|m_A - n_B|$ eigenvalues of zero occur. Applications related to the total bond orders of effective bonds in equilibrium situations of molecules to their corresponding bond lengths were given. Diatomic molecules and hydrogen bonding were also discussed.

In this paper we want to demonstrate the usefulness of this new bond order principle by illustrating some of the details. In the next section, figures of the bond order orbitals are presented for CC bonds. For bonds between C, N, and O atoms the contributions to the total bond order are given for a number of representative cases.

II. Bond Order Orbitals

From the previous paper¹ and remarks in the Introduction it is clear that the diagonalization of the two-center parts of the density matrix yields two-center orbitals distinctly different from the MOs which extend over the whole molecule:

$$\begin{aligned} b_i &= g_i + h_i \\ &= \bar{g}_i + \bar{h}_i \end{aligned} \quad (2.1)$$

It should be emphasized here that even after deorthogonalization of the symmetrically orthogonalized form $g_i + h_i$ no other centers than the two considered are involved. The form of eq 2.1 has a striking resemblance to the pairs of directed hybrids of sp , sp^2 , or sp^3 type which are frequently used to illustrate directed valence in molecules. So after transformation

of MOs to localized orbitals the situation would become more comparable to that of bond order orbitals. Yet it is not completely convertible since we know that π MOs in conjugated systems cannot in general be localized. This means that a single π AO has to be used for the description of the bonding to several adjacent atoms. There is no unique subdivision into exclusive subsets of π orbitals. Yet in σ bonding such a subdivision is common practice. Let us take as an example the acetylene molecule. The simplest localized description for the σ system is $b_{CH} = sp_C + s_H$ and $b_{CC} = sp_C + sp_C$. Our connotation is that CC σ bonding is not only formed by the hybrid pair of sp hybrids directed toward each other, but also influenced by the pair of sp hybrids directed toward the H atoms. In a minimal basis set we obtain four orthogonal bond order orbitals of the form

$$\begin{aligned} b_1 &= a_1s_A + a_2pz_A + a'_1s_B + a'_2pz_B \\ b_2 &= a_3s_A + a_4pz_A + a'_3s_B + a'_4pz_B \\ b_3 &= c_1px_A + c'_1px_B \\ b_4 &= c_2py_A + c'_2py_B \end{aligned} \quad (2.2)$$

if we use a localized axis system and σ and π can be separated. If no such separation is possible mixtures of the above b_i will occur. It should be stressed that the localized description in σ and π does not influence the actual form of the bond order orbitals. This depends totally on the form of the density matrix, since the method is invariant under coordinate transformations.

In the following figures three-dimensional plots and contour lines for CH and CC bonds are presented based on SINDO calculations.³ Figure 1 shows CH bonds of acetylene, ethylene, ethane, and cyclopropane. The p character in the first three bond orbitals is greater than 1, 2, or 3, respectively, but in the expected order. Cyclopropane is hybridized toward H as acetylene. The bond orders are close to one. Figures 2-7 analyze the CC bond of acetylene, ethylene, ethane, cyclopropane, *trans*-butadiene, and vinyl anion. There are essentially two σ and two π bond orbitals. The nodeless σ bond orbital concentrates charge in the bonding region and is the equivalent to the description of pair bonds in the localized σ system. However, the corresponding bond order is not unity, but slightly lower than one. Only in acetylene, ethylene, and ethane are they purely of σ character. The mixture with π is well pronounced in cyclopropane and vinyl anion, very little in *trans*-butadiene. We understand that in cyclopropane a bent bond is necessary for mathematical reasons, namely, because of the impossibility of construction of two orthogonal hybrids directed along two adjacent CC bonds separated by 60° . But mixing occurs also in *trans*-butadiene, because symmetry does not prohibit mixing of local σ and π which is defined in the molecular plane. Hence bond orbitals are in general not directed along the internuclear axes, and bent bonds seem to be the normal case. The second σ bond orbital contains one nodal surface, which is not planar in the latter three molecules. The bond order contribution is

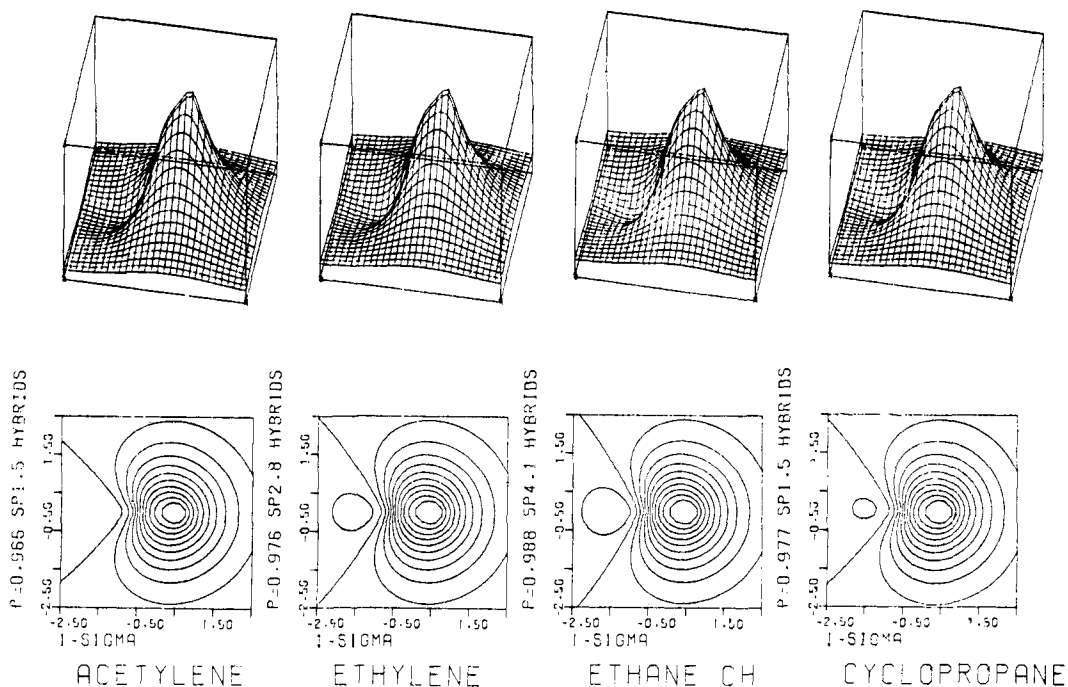


Figure 1. Bond order orbital plots and contour diagrams for CH bonds in acetylene, ethylene, ethane, and cyclopropane. Distances along the abscissa are in Ångstroms.

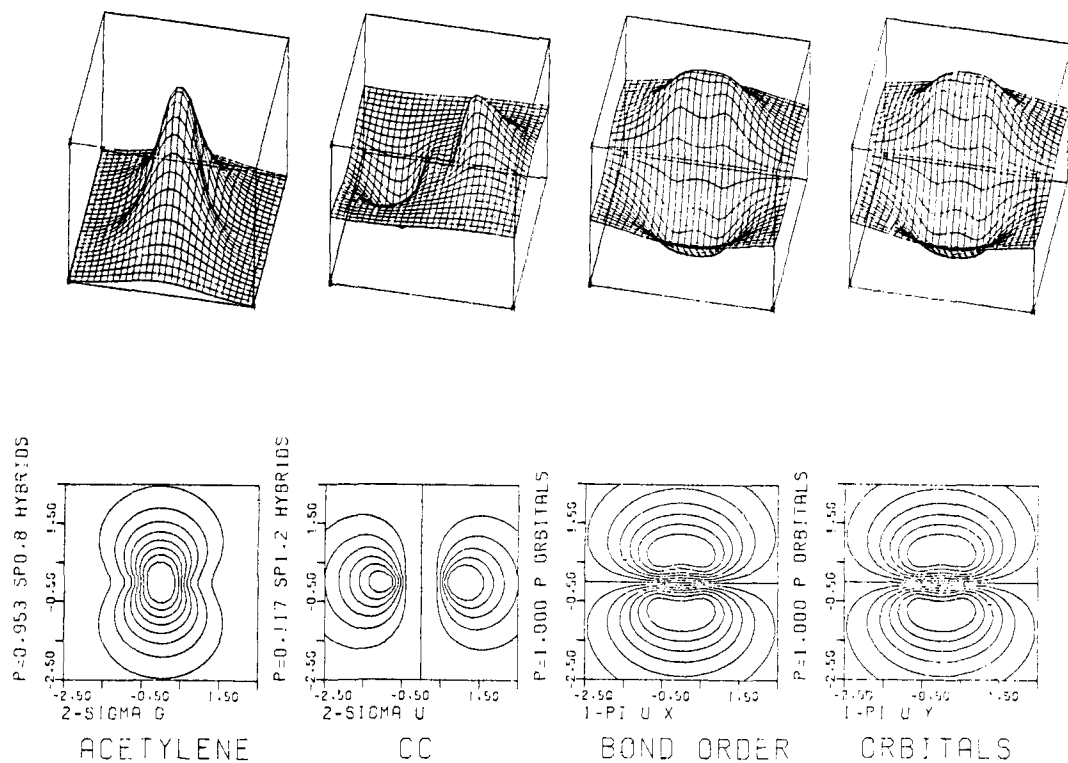


Figure 2. Same as in Figure 1 for CC bonds in acetylene.

usually negative because of the antibonding character of that orbital. The exception is acetylene, where this orbital is bonding. A comparison shows that in this case the hybrids contain significantly more p character than in the other molecules. Bent bonds show in cyclopropane and *trans*-butadiene and are markedly more visible in vinyl anion. The π bonding contains large contributions of one or close to one if there is a "real" π system as in acetylene, ethylene, *trans*-butadiene, and vinyl anion. In addition, small corrective contributions from π components occur in all molecules except acetylene which

were neglected previously since they were considered as belonging to localized σ bonds with other atoms. These small components are degenerate in ethane. In cyclopropane the π contribution in the carbon plane is quite significant and increases the total bond order beyond the value of a normal single bond. Again the bent bond character is quite pronounced in cyclopropane and vinyl anion, and also in *trans*-butadiene.

The figures presented here were based on SCF calculations. CI calculations are necessary to describe the bonding in *o*-ethylene. The total wave function is expanded in configurations

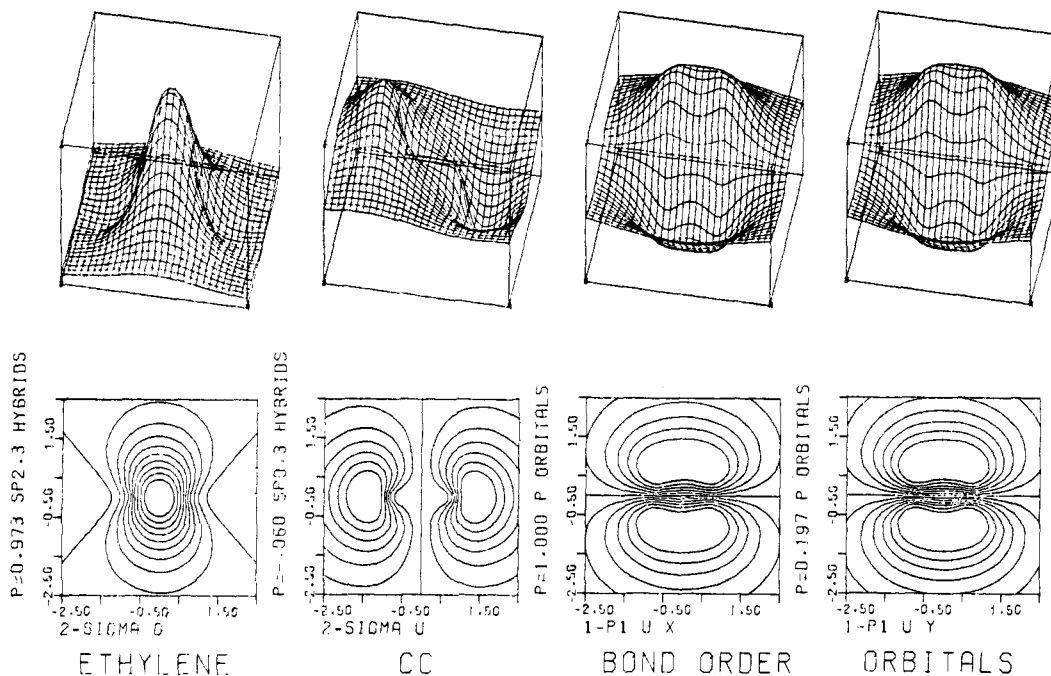


Figure 3. Same as in Figure 2 in ethylene.

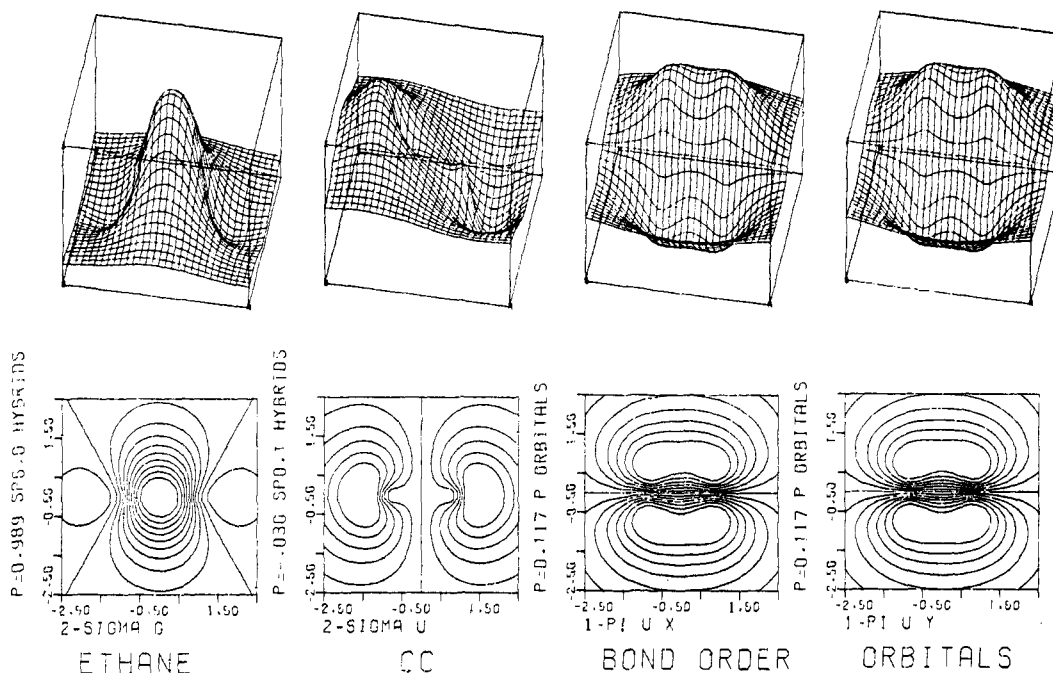


Figure 4. Same as in Figure 2 in ethane.

Ψ_I consisting of MOs.

$$\Psi = \sum_I A_I \Psi_I$$

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

$$\Psi_I = (N!)^{-1/2} \det|\psi_{i_1} \psi_{i_2} \dots \psi_{i_N}|$$

The density operator is then given as⁴

$$P_{op} = |\Psi\rangle\langle\Psi|$$

$$= \sum_{I,J} A_I A_J |\Psi_I\rangle\langle\Psi_J|$$

$$= \sum_{I,J} A_I A_J \sum_{i,j} \rho_{IJij} |\psi_i\rangle\langle\psi_j|$$

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

We then obtain

$$P_{op} = \sum_I A_I^2 \sum_{i,i'} |\psi_{i_i}\rangle\langle\psi_{i_i}| + \sum_{\substack{I,J \\ I \neq J}} A_I A_J (-1)^{s-t} |\psi_{i_s}\rangle\langle\psi_{j_t}|$$

$$P_{AB} = Tr(\mu_A | P_{op} | \nu_B)$$

With expansion of the MOs ψ_i in orthogonalized AOs μ

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

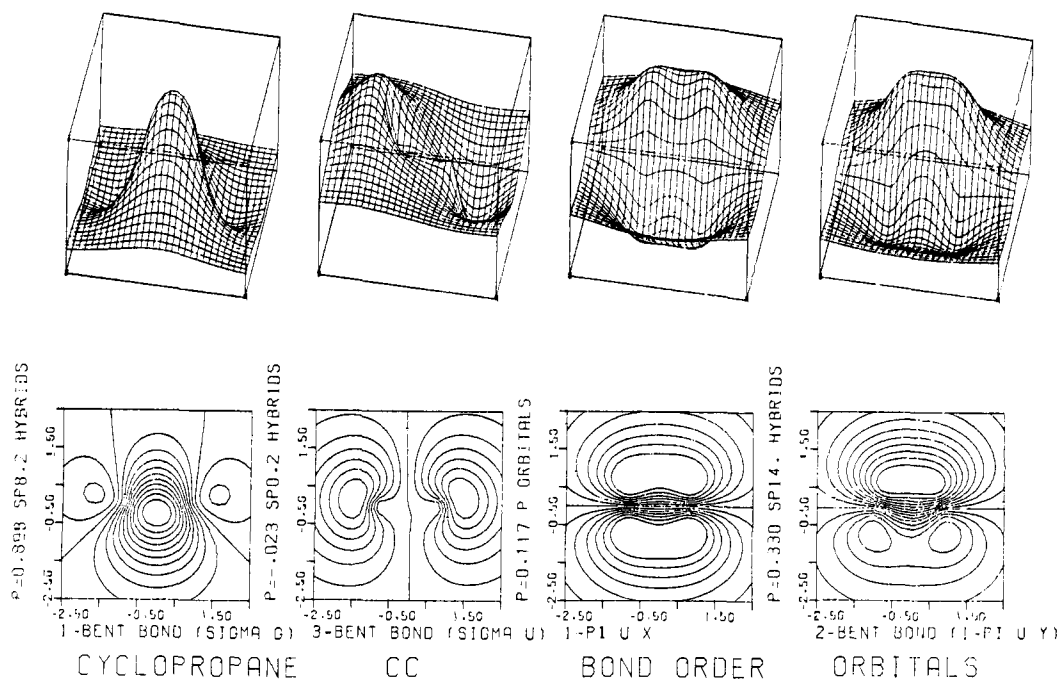
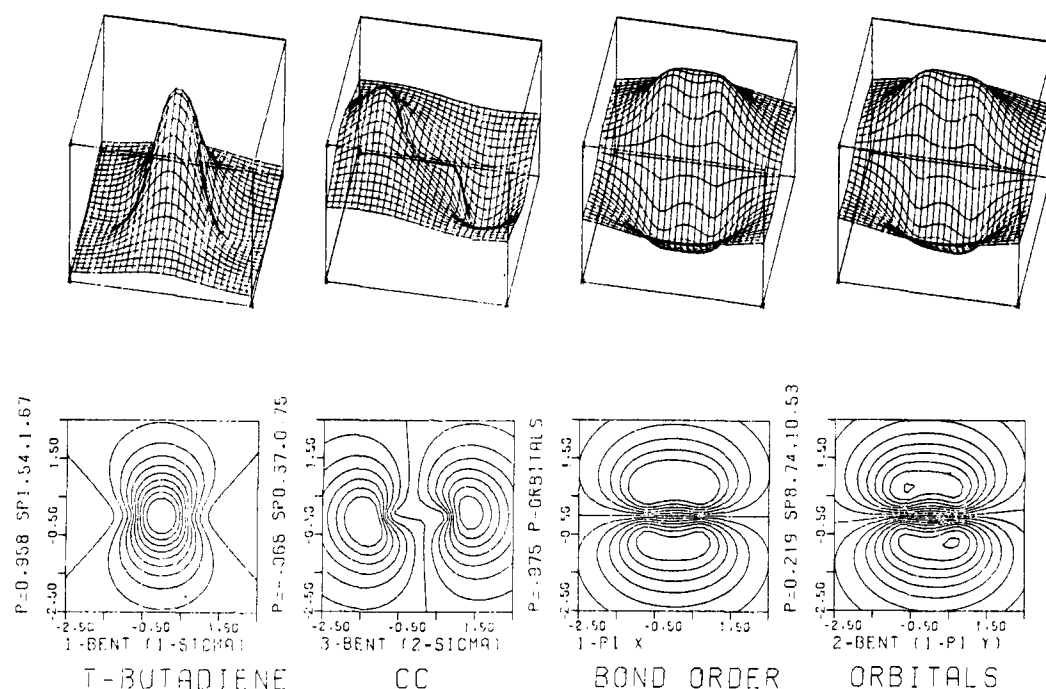


Figure 5. Same as in Figure 2 in cyclopropane.

Figure 6. Same as in Figure 2 in *trans*-butadiene.

we finally obtain

$$P_{AB} = \text{Tr}(P_{\mu_A \nu_B}) \quad (2.3)$$

$$\text{with } P_{\mu_A \nu_B} = \sum_I A_I^2 \sum_{ij} c_{i\mu_A} c_{j\nu_B} + \sum_{I, J} A_I A_J c_{i\mu_A} c_{j\nu_B} \quad i \neq j$$

With eq 2.3 *o*-ethylene is correctly described by a single CC bond, whereas it appears with a double bond in the SCF formalism.

III. Bond Order Eigenvalues

Formula 1.1 describes the total bond order as a sum of eigenvalues multiplied by the overlap integral of the corre-

sponding bond order orbital hybrids. In Table I we have listed these products for SINDO wave functions for a variety of representative molecules. Closed- and open-shell cases are included as well as neutral molecules, ions, and radicals with single, double, and triple bonds between C, N, and O atoms. The bond order orbitals are of the form of eq 2.2 or mixtures of those. We recognize that the conventional view of localized bonding is represented by the eigenvalue belonging to bond orbital $2\sigma_g$. They are not unity, except in N_2 , even in systems with homopolar bonds. CC bond values are usually between 0.9 and 1.0, although in some ions (C_2H^+ , C_2H^-) and radicals (C_2H , C_2) and systems with adjacent CO bonds (ketene, diketene) even considerably lower values might occur. In the other homopolar (NN, OO) and heteropolar (CN, CO,

Table I. Bond Order Eigenvalues for Molecules Containing C, N, and O Atoms^a

molecule	bond	total bond order	bond order orbital			
			$2\sigma_g$	$2\sigma_u$	$1\pi_x$	$1\pi_y$
cyclobutane	CC	1.097	0.975*	-0.061*	0.112	0.071*
diketene		1.142	0.846*	0.086*	0.138	0.072*
ethane		1.193	0.989	-0.030	0.117	0.117
propene		1.209	0.959*	-0.036*	0.160*	0.126*
<i>trans</i> -butadiene		1.241	0.930*	-0.046*	0.220*	0.137*
cyclopropane		1.322	0.898*	-0.023*	0.117	0.330*
C ₂ H ₅ ⁺		1.332	0.925*	-0.032*	0.314	0.125*
C ₂ H ₅ ⁻		1.335	0.927*	-0.044*	0.136	0.316*
C(CH ₂) ₃		1.439	0.888	-0.055	0.439	0.166
allyl		1.493	0.886*	-0.050*	0.497	0.160*
benzene		1.736	0.944*	-0.061*	0.667	0.186*
ketene		1.928	0.854	0.089	0.758	0.227
allene		2.070	0.959	-0.080	0.940	0.251
<i>trans</i> -butadiene		2.084	0.958*	-0.068*	0.975	0.219*
propene		2.097	0.961*	-0.068*	0.986*	0.218*
ethylene		2.110	0.973	-0.060	1.000	0.197
C ₂ H ₃ ⁻		2.137	0.945*	-0.096*	0.986	0.302*
diketene		2.164	0.914*	0.088*	0.927	0.235*
C ₂ H ₃ ⁺		2.306	0.946	-0.068	0.994	0.434
acetylene		3.070	0.953	0.117	1.000	1.000
C ₂ H ⁺		3.076	0.710	0.556	1.000	0.810
C ₂ H		3.093	0.825	0.276	0.996	0.996
C ₂ H ⁻		3.115	0.877	0.238	1.000	1.000
C ₂		3.456	0.728	0.728	1.000	1.000
H ₂ NCN	CN	1.348	0.930*	-0.050*	0.300	0.168*
HNC		2.708	0.904*	-0.110*	0.957*	0.957*
NCCN		2.716	0.947	-0.199	0.984	0.984
NCO ⁻		2.723	0.957	-0.102	0.934	0.934
HNCO		2.766	0.923*	0.093*	0.875*	0.875*
HCN		2.817	0.972	-0.147	0.996	0.996
H ₂ NCN		3.071	0.952	0.201	0.939	0.979
CN		3.095	0.795	0.334	0.983	0.983
CN ⁺		3.476	0.837	0.693	0.973	0.973
H ₃ COH	CO	1.261	0.964	-0.033	0.180	0.151
NCO ⁻		1.434	0.918	-0.080	0.298	0.298
HNCO		1.778	0.867*	0.139*	0.386*	0.386*
CO ⁺		2.140	0.714	-0.296	0.861	0.861
CO ₂		2.148	0.945	-0.097	0.650	0.650
H ₂ CO		2.199	0.975	-0.053	0.980	0.297
HCO		2.281	0.896*	-0.059*	0.885	0.558*
CO		2.760	0.908	0.000	0.926	0.926
HCO ⁺		2.768	0.958	-0.066	0.938	0.938
N ₂ O ₄	NN	0.234	0.180*	-0.047*	0.061	0.040*
N ₂ H ₄		1.353	0.982*	-0.044*	0.208*	0.207*
HN ₃		1.706	0.900*	-0.067*	0.545	0.329*
N ₂ H ₂		2.255	0.995*	0.038*	1.000	0.222*
N ₃ ⁻		2.281	0.929	-0.062	0.707	0.707
HN ₃		2.673	0.960*	-0.062*	0.838	0.937*
NNO		2.732	0.957	-0.069	0.922	0.922
N ₂		3.000	1.000	0.000	1.000	1.000
NNO	NO	1.606	0.900	-0.066	0.386	0.386
N ₂ O ₄		1.995	0.894*	-0.051*	0.698	0.454*
NO ₂		2.003	0.900*	-0.054*	0.697	0.460*
NO		2.417	0.982	0.0002	0.966	0.469
HNO		2.816	0.994*	0.000*	0.996	0.196*
NO ⁺		2.929	0.977	0.000	0.976	0.976
H ₂ O ₂	OO	1.194	0.996*	0.000*	0.099*	0.099*
O ₃		1.759	0.927*	0.000*	0.707	0.125*
O ₂		2.000	0.999	0.001	0.500	0.500

^a Values marked with an asterisk belong to orbitals which are mixtures of σ and π . The subscripts g and u do not apply in cases without inversion symmetry.

NO) the picture is basically the same. The only remarkable exception is N₂O₄, with a value of 0.180 for the NN bond, the total bond order of 0.234 not being much larger. So N₂O₄ appears as two NO₂ molecules held very weakly together.

The bonding σ bond contribution obtains a correction from the outer σ hybrids which form another pair. This bond orbital has one node and is usually antibonding with the bond eigenvalue being quite small. So the correction is negative in most

cases. There are some remarkable exceptions, though, notably in CC and CN bonds. For ketene, diketene, and acetylene values are in the order of 0.1. C₂ and CN⁺ have a much larger value of the same magnitude as the $2\sigma_g$ value. Here it is of great importance whether the overlap of $2\sigma_u$ is positive or negative. Only an investigation of the basis set dependence could clarify the situation. An analysis of Ransil's⁵ C₂ minimal basis wave function was inconclusive, yielding a positive overlap for Slater

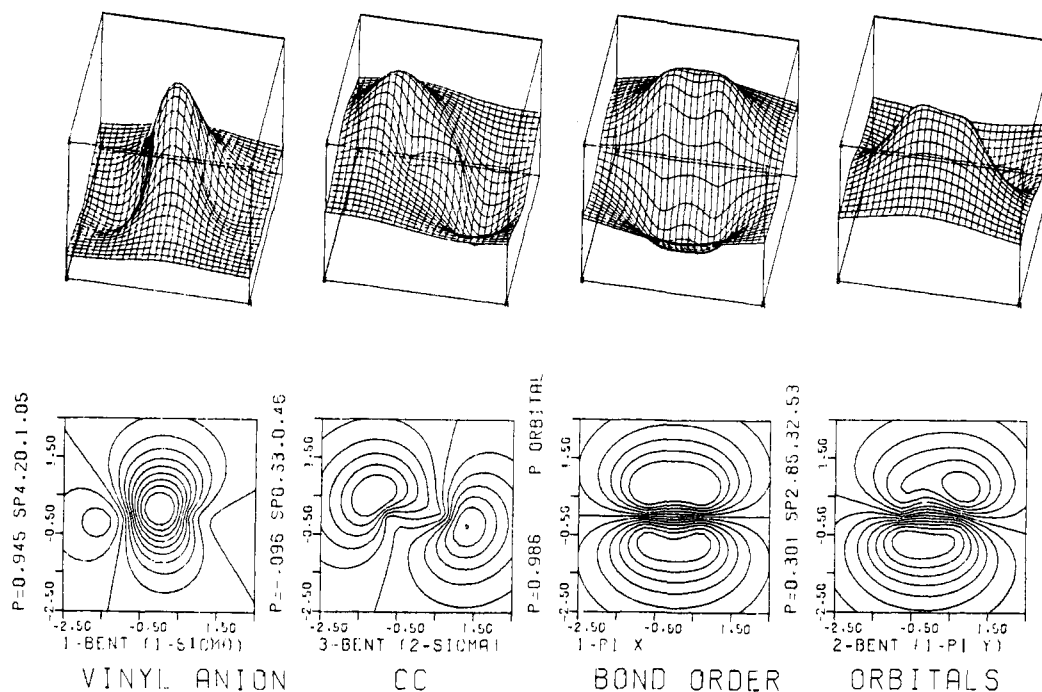


Figure 7. Same as in Figure 2 in vinyl anion.

and best atom AOs and a negative overlap for best limited AOs. In this case the bond order varies between a triple and a double bond.⁶ The third contribution is from the bonding perpendicular to the plane if such a plane exists. In the latter case it conforms to the standard π MO bond order by Coulson.⁷ Hyperconjugation can modify this standard value, though, such as it does in propene where it reduces the "localized" π bond from 1 to 0.986. The majority of cases can be grouped into groups with values close to one and values close to zero. The latter are always positive and occur in cases where π bonding is conventionally neglected as in ethane, cyclobutane, or cyclopropane. The last column contains the second possibility for π bonding. The values are sizable only in molecules with linear chains. However, these π contributions are not necessarily negligible in other cases. In cyclopropane, the in-plane π bonding is the reason for the larger total bond order compared to ethane and consequently for the smaller bond length, since bond order and bond length have an approximately linear relationship.¹

IV. Conclusion

The new bond order principle appears as a helpful tool to understand the chemical bond. Bond order orbitals can be

presented to illustrate the covalent part of bonding. The conventional view of σ and π bonding is included in this picture by the dominating hybrid terms. The corresponding eigenvalues of these terms constitute the main part of the total bond order. However, correction terms from other hybrid pairs are not negligible. A formulation of the method for CI wave functions is also presented.

Acknowledgment. I thank Dr. C. P. D. Dwivedi and Mr. H. W. Krüger for performing some of the calculations. This research was supported by a grant from Deutsche Forschungsgemeinschaft. Computer time was furnished by TU Hannover.

References and Notes

- (1) K. Jug, *J. Am. Chem. Soc.*, **99**, 7800 (1977).
- (2) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955).
- (3) P. Coffey and K. Jug, *J. Am. Chem. Soc.*, **95**, 7575 (1973).
- (4) E. R. Davidson, "Reduced Density Matrices in Quantum Chemistry", Academic Press, New York, N.Y., 1976, p 31.
- (5) B. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960).
- (6) K. Jug, unpublished results.
- (7) C. A. Coulson, *Proc. R. Soc. London, Ser. A*, **169**, 419 (1939).