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Short Communication

On the Bond Order of C_2 and N_2

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The commonly adopted bond order values of C_2 and N_2 are critically investigated with a new bond order concept. *Ab initio* calculations with extended basis sets suggest that C_2 can be described by a double to triple bond closer to acetylene than to ethylene and N_2 by a triple bond. The basis set dependence is discussed. Also a relation between the number of basis functions, MO's and non-vanishing eigenvalues of the bond order parts of the density matrix is presented.

Key words: Bond order of C_2 and N_2

Homonuclear diatomic molecules serve as primary examples to introduce the efficiency of the bond order concept in the Aufbau principle. Their textbook value was firmly established by Coulson [1]. In the Aufbau principle σ_g and π_u MO's are bonding and σ_u and π_g MO's antibonding. This assessment comes from the simplified MO form which uses combinations of s AO's on one hand and p AO's on the other hand without mixing. In this description, C_2 is bound by a double bond formed by two perpendicular π bonds whereas the σ bond contributions cancel. N_2 has a triple bond with one σ and two π bonds. The most elementary form of mixing s and p is called hybridization. Under this mixing it is no longer clear what bonding and antibonding means. In this case, there is no natural atomic reference state available such as s and p. Mulliken suggested that bonding should mean positive overlap of hybrids on the two centers and antibonding negative overlap [2]. To preserve the simple picture one could sum up over certain elements of the charge and bond order matrix. In the minimal basis set one could take, e.g., the following sum as the bond order:

$$P_{AB} = P_{s_A s_B} + P_{p\sigma_A p\sigma_B} + P_{p\pi_A p\pi_B} + P_{p\bar{\pi}_A p\bar{\pi}_B}.$$

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This would result again in a double bond for C_2 and a triple bond for N_2. However, here we do not know how to assess the influence of *s* and *p* mixing. The incentive for the subsequent study was our doubt that C_2 should be described without any σ bonding. We used a method recently developed by Jug [3]. Here the bond order appears as the sum of eigenvalues of the respective parts of the bond order matrix. The Mulliken criterion [2] was used to determine the bonding or antibonding character of the bond order orbitals accompanying the eigenvalues. After discovery of discontinuities [4] arising from this criterion, the Mulliken concept was replaced by a vector projection technique [5]. To avoid the criticism of basis set dependence of our results, we used three levels of bases: minimal, double zeta, and triple zeta. Density matrices of *ab initio* SCF calculations were analyzed with our maximum bond order concept [3]. Table 1 contains the results obtained by the minimal basis set SCF wavefunctions generated by Ransil [6]. No problem arises for N_2 where the bond order is uniformly 3 regardless of basis set and weighting factor. For C_2 the Mulliken overlap criterion predicts a bond order of 3.8 or 2.0 depending on whether the second occupied σ MO is bonding or antibonding in the Mulliken sense. The vector projection technique always predicts a bond order of 2 or very close to it. Since we have previously made a case [5] for the second procedure of weighting, it would seem natural to adopt the value of 2 for the bond order of C_2. We will show in the following that this conclusion would be ill-considered. Since there is controversy in this case, clarification must be through more extended SCF

Table 1. Bond orders of minimal basis set SCF calculations on C_2 and N_2

	C_2			N_2		
Basis	Eigenvalue	Overlap factor	Projection factor	Eigenvalue	Overlap factor	Projection factor
Slater	1.000	1.0	1.0	1.000	1.0	1.0
	1.000	1.0	1.0	1.000	1.0	1.0
	0.895	1.0	−1.0	1.000	1.0	1.0
	0.895	1.0	1.0			
	Total bond order:	3.790	2.000	Total bond order:	3.000	3.000
Best atom	1.000	1.0	1.0	1.000	1.0	1.0
	1.000	1.0	1.0	1.000	1.0	1.0
	0.908	1.0	−1.0	1.000	1.0	1.0
	0.907	1.0	1.0			
	Total bond order:	3.815	1.999	Total bond order:	3.000	3.000
Best limited	1.000	1.0	1.0	1.000	1.0	1.0
	1.000	1.0	1.0	1.000	1.0	1.0
	0.821	−1.0	−1.0	1.000	1.0	1.0
	0.820	1.0	1.0			
	Total bond order:	1.999	1.999	Total bond order:	3.000	3.000

Table 2. Bond orders of extended basis set SCF calculations on C_2 and N_2

	C_2			N_2		
Basis	Eigenvalue	Overlap factor	Projection factor	Eigenvalue	Overlap factor	Projection factor
Double zeta	—	—	—	1.0	1.0	1.0
	1.0	1.0	1.0	1.0	1.0	1.0
	1.0	1.0	1.0	1.0	1.0	1.0
	0.9696	1.0	0.3578	0.6961	1.0	1.0
	0.9696	1.0	0.3617	0.6961	−1.0	−1.0
	0.0975	−1.0	0.3274	0.0041	−1.0	−1.0
	0.0975	−1.0	−0.3770	0.0041	1.0	1.0
	Total bond order:	3.744	2.693	Total bond order:	3.000	3.000
Triple zeta	—	—	—	1.0	1.0	1.0
	1.0	1.0	1.0	1.0	1.0	1.0
	1.0	1.0	1.0	1.0	1.0	1.0
	0.9641	1.0	−0.0018	0.7427	1.0	0.9985
	0.9641	1.0	0.6751	0.7427	−1.0	−0.9984
	0.1201	−1.0	−0.3022	0.0849	−1.0	−0.6034
	0.1201	−1.0	0.1485	0.0849	−1.0	0.6035
	Total bond order:	3.688	2.631	Total bond order:	2.830	3.000

calculations on the *ab initio* level. We used basis sets of 64 Gaussians contracted to 20 basis orbitals representing double zeta quality and 78 Gaussians contracted to 28 basis orbitals representing triple zeta quality except for the 1*s* orbitals [7]. Table 2 shows the bond order for C_2 and N_2 in these basis sets. Here the bond order based on overlap weighting shows the serious discontinuity problem in N_2 and should finally be abolished. The vector projection technique shows no basis set dependence in N_2 and only a slight basis set dependence in C_2. Our suggestion therefore would be to describe C_2 by the bond order 2.63 and N_2 by 3. Whereas the result for N_2 is not surprising, the C_2 bond order needs a few more sentences of explanation. In the minimal basis set the occupation of MO's is such that it creates one bonding and one antibonding bond order orbital. The degeneracy or quasi-degeneracy of the respective eigenvalues generates parallel or antiparallel vectors in the Hilbert space. There are not enough degrees of freedom for other orientations. As soon as the basis set is extended the weighting procedure can adjust the σ contributions by weighting factors between 0 and 1.

From Table 2 we also see that the number of nonvanishing eigenvalues of the two-center parts of the bond order matrix varies with the number of basis orbitals. We tentatively suggest a formula to describe this fact. If N_A and N_B denote the number of basis orbitals on atoms A and B, N^{occ} and N^{unocc} the number of occupied and unoccupied MO's, the number of nonvanishing eigenvalues N should be

$$N = \mathrm{Min}\,(N^{occ}, N^{unocc}, N_A, N_B).$$

This relation was observed in closed-shell and restricted open-shell cases for various molecules.

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