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Comparative Studies on a Maximum Bond Order Principle

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A recently proposed maximum bond order principle is studied with respect to choice of basis orbitals, choice of wavefunction and compared with other methods. Results for bond orders support the choice of Schmidt orthogonalized AO's with subsequent Löwdin orthogonalization. Differences between semiempirical and *ab initio* wavefunctions in minimal basis sets usually have only minor effects on bond order values. For hydrocarbons bond order values are quite similar for Cohen's and this method. Finally, the dependence of bond orders on internal rotation and vibration is investigated in a few simple cases.

Key word: Bond orders

1. Introduction

Recently we proposed a new bond order principle [1] which appears as a sum of eigenvalues of the two-center part of the related density matrix of each pair of atoms in a molecule. The underlying idea was to select pairs of hybrids from each of the two atoms considered so that the bond order would be as large as possible within a predetermined SCF MO set. The procedure amounts to a local orthogonal transformation of basis orbitals within the SCF wave function built from an atomic basis set centered on the atoms. The definition was general enough to include nonbonding and antibonding effects. Its applicability to any type and size of AO basis sets as well as to open shell and CI wavefunctions was stressed. The CI form was formulated in a subsequent paper [2]. Applications demonstrated the usefulness of the principle not only for standard bonds, but also for hydrogen bonds and reactions. A linear relation could be approximately established between bond order and bond length [2]. This relation had been documented earlier only for π-systems [3]. We then compared the eigenvalues and their related eigenvectors,

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which we called bond order orbitals, and demonstrated that the popular directed hybrids in a description of localized bonding are a special case where corrective contributions from further hybrid pairs, centered on the two atoms considered, were neglected [2].

Several questions had arisen in the course of this work. How would the kind of atomic orbitals influence the bond order values? Are there significant differences between bond orders calculated with semiempirical or *ab initio* wavefunctions? How does our bond order principle compare with other concepts? How do bond orders change with distortions in molecules? In the following sections we try to answer these questions. Section 2 shows the differences in bond order values between non-orthogonal, locally and globally orthogonalized Slater-type AO's. Then a comparison is made for bond order calculated in minimal basis sets by semiempirical and *ab initio* methods at optimized or experimental geometries. Since we had previously shown that Coulson's [5, 6] and Mulliken's [7] bond order definitions lack general applicability, we picked only Cohen's [8] method for comparison. In Section 3, the variation of bond orders in internal rotations is studied in ethane and hydrazine. Subsequently, effects of bond length and bond angle changes on bond orders are presented for ethane, ethylene, acetylene and allene.

2. Analysis of Method

It is obvious that the density matrix P depends on the type of atomic orbitals used. We had suggested that the atomic basis should be Schmidt orthogonalized on each atom and then symmetrically orthogonalized [9] over the whole molecule. We call this procedure global orthogonalization. It is also possible to define the density matrix on a locally orthogonalized set which is Schmidt orthogonalized on each atom and where symmetrical orthogonalization is performed separately for each atom pair whose bond order is considered. Finally a non-orthogonal Slater basis set can be used for construction of P. For the last case, we know already from Mulliken's work [7] that values for $P_{\mu\nu}$ can be much smaller than unity for single bonds.

In Table 1 we present the results for CC and NN bond orders based on calculations on selected molecules. The minimal basis *ab initio* SCF wavefunctions were generated by Müller [10] with Slater exponents at experimental geometries and by Fliszar [11] with optimized exponents at optimized geometries. It is apparent from the bond order values that non-orthogonal basis sets are rather unsuitable to define bond orders within our maximum bond order principle. Their values are much smaller than in common usage. Locally and globally orthogonalized sets furnish acceptable values. The former are a few percent larger than the latter. For CH bonds the situation is basically the same. A typical example is ethylene, where the CH bond order values are 0.610 for a non-orthogonal set, 1.045 for a locally orthogonalized set and 0.989 for a globally orthogonalized set with Müller's wavefunction. Since values for the globally orthogonalized set are closest to the standard terminology, this set seems most appropriate for further use. Support to this choice

Table 1. Comparison of AA bond orders calculated on different AO bases

	Experimental geometry Müller [10]					Optimized geometry Fliszar [11]			
Molecule	Bond length Å		AO basis	local OAO basis	global OAO basis	Bond length Å	AO basis	local OAO basis	global OAO basis
C_2H_2	1.205	C–C	2.077	3.082	3.065				
C_2H_4	1.336		1.279	2.169	2.117	1.318	1.340	2.170	2.116
$s\text{-}C_2H_6$	1.536		0.504	1.267	1.194	1.524	0.603	1.239	1.173
$e\text{-}C_2H_6$	1.536		0.478	1.244	1.163				
C_3H_4	1.308		1.342	2.225	2.150				
C_3H_6	1.510		0.487	1.261	1.209	1.493	0.554	1.231	1.206
C_3H_8						1.530	0.610	1.249	1.174
$n\text{-}C_5H_{12}$						1.535	0.617	1.249	1.174
C_6H_6						1.395	1.067	1.833	1.753
C_6H_{12}						1.532	0.614	1.260	1.175
$c\text{-}N_2H_4$	1.451	N–N	0.329	1.116	1.055				
$o\text{-}N_2H_4$	1.451		0.518	1.309	1.163				
$t\text{-}N_2H_4$	1.451		0.391	1.191	1.141				

Table 2. Comparison of AA bond orders calculated by different methods

	Jug's Method [1]								Cohen's Method [8]			
	ab initio calculation				semiempirical calculation				*ab initio* calculation			
	exp. geometry Müller [10]		opt. geometry Fliszar [11]		exp. geometry		opt. geometry		exp. geometry Müller [10]		opt. geometry Fliszar [11]	
Molecule	R(Å)	P	R(Å)	P	R(Å)	P	R(Å)	P	R(Å)	P	R(Å)	P
C_2H_2	1.205	3.065			1.205	3.103	1.304	3.071	1.205	2.898		
C_2H_4	1.336	2.117	1.318	2.116	1.336	2.170	1.486	2.110	1.336	1.989	1.318	2.027
s-C_2H_6	1.536	1.194	1.524	1.173	1.536	1.307	1.713	1.201	1.536	1.022	1.524	1.126
e-C_2H_6	1.536	1.163			1.536	1.294	1.716	1.186	1.536	0.992		
C_3H_4	1.308	2.150			1.308	2.318	1.478	2.069	1.308	2.100		
C_3H_6	1.510	1.209	1.493	1.206	1.510	1.104	1.684	1.321	1.510	1.421	1.493	1.321
C_3H_8			1.530	1.174	1.533	1.304	1.706	1.203			1.530	1.152
n-C_5H_{12}			1.535	1.178	1.539	1.284	1.710	1.191			1.535	1.170
C_6H_6			1.395	1.753	1.397	1.826	1.564	1.735			1.395	1.700
C_6H_{12}			1.532	1.175	1.528	1.312	1.706	1.205			1.532	1.170
c-N_2H_4	1.451	1.056			1.451	1.137			1.451	0.953		
o-N_2H_4	1.451	1.163			1.451	1.267			1.451	1.091		
t-N_2H_4	1.451	1.141			1.451	1.196			1.451	0.939		

Table 3. Comparison of AH bond orders calculated by different methods

Molecule	Jug's Method [1]								Cohen's Method [8]			
	ab initio calculation				semiempirical calculation				*ab initio* calculation			
	exp. geometry Müller [10]		opt. geometry Fliszar [11]		exp. geometry		opt. geometry		exp. geometry Müller [10]		opt. geometry Fliszar [11]	
	R(Å)	*P*	*R*(Å)	*P*	*R*(Å)	*P*	*R*(Å)	*P*	*R*(Å)	*P*	*R*(Å)	*P*
CH_4			1.083	0.999	1.083	0.998	1.184	0.995			1.083	1.064
C_2H_2	1.059	0.988			1.059	0.971	1.158	0.966	1.059	0.994		
C_2H_4	1.103	0.989	1.080	0.992	1.103	0.976	1.176	0.976	1.103	1.067	1.108	1.054
s-C_2H_6	1.107	0.993	1.094	0.996	1.107	0.987	1.183	0.988	1.107	1.075	1.094	1.062
e-C_2H_6	1.107	0.994			1.107	0.987	1.183	0.988	1.107	1.077		
C_3H_4	1.087	0.981			1.087	0.966	1.183	0.968	1.087	1.049		
C_3H_6	1.089	0.990	1.087	0.993	1.089	0.976	1.172	0.977	1.089	1.066	1.087	1.054
C_3H_8			1.097	0.992	1.096	0.977	1.184	0.981			1.097	1.056
			1.094	0.996	1.097	0.983	1.184	0.985			1.094	1.062
			1.093	0.995	1.097	0.986	1.184	0.988			1.093	1.067
n-C_5H_{12}			1.093	0.995	1.120	0.983	1.184	0.985			1.093	1.063
C_6H_6			1.090	0.990	1.084	0.954	1.177	0.963			1.090	1.055
C_6H_{12}			1.103	0.991	1.119	0.968	1.184	0.976			1.103	1.053
			1.102	0.992	1.119	0.975	1.184	0.981			1.102	1.058
c-N_2H_4	1.022	0.990			1.022	0.986			1.022	1.028		
o-N_2H_4	1.022	0.987			1.022	0.984			1.022	1.030		
t-N_2H_4	1.022	0.988			1.022	0.986			1.022	1.026		

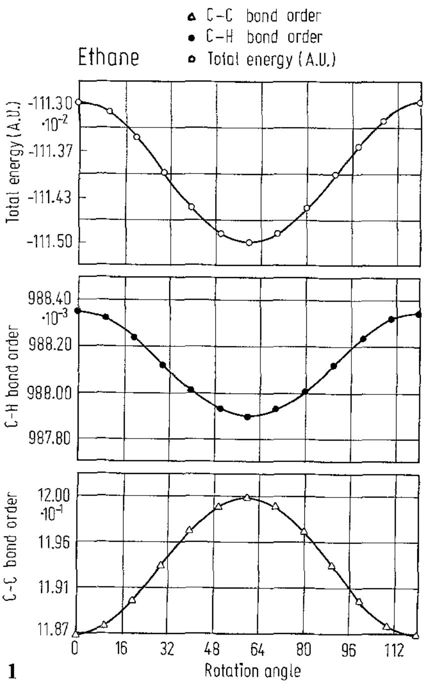
is also given by the fact that a locally orthogonalized set does not conserve the total charge.

Next we attempted a preliminary comparison of semiempirical and *ab initio* methods. Since semiempirical methods use minimal basis sets, we chose this type of set also for *ab initio* calculations. The latter includes also 1*s* orbitals. Table 2 shows the differences between *ab initio* and semiempirical bond order values at experimental and optimized geometries. The differences for the latter comparison are quite small in *ab initio* wavefunction and larger in semiempirical calculations. These were done with the SINDO method which overestimated bond lengths by 10% [12]. Most gratifying is that differences between optimized *ab initio* and optimized semiempirical bond order values are usually slight. They are appreciable only in allene, cyclopropane and hydrazine. Within each scheme consistency is conserved which means bond orders are linearly decreasing with increasing bond lengths. Table 3 lists CH and NH bond orders for comparison. Here the differences between *ab initio* and semiempirical methods or experimental and optimized geometries are even less pronounced than in CC or NN bonds. In Tables 2 and 3, bond order values after Cohen [8] are also presented. Cohen uses a projection technique for polyatomics in conjunction with one of Mulliken's diatomic methods [7]. Cohen's values are most convincing in homopolar bonds except in cyclopropane where the CC bond order at experimental geometry seems excessively large. For heteropolar bond differences between this method and Cohen's method can be more pronounced. In HF he found a bond order of 0.63 [8], whereas we found a value of 0.95 [1]. Cohen's small value can be attributed to the way in which he rescales the density matrix value on non-orthogonal orbitals by overlap. His approach is overlap population dependent. We, on the other hand, let the covalent bond order find its largest value within a given SCF wavefunction.

3. Comparison of Bond Order and Experimental Quantities

Here we present the application of the bond order method to internal rotation and vibration. Fig. 1 shows the dependence of total energy and CC and CH bond orders on the torsion angle in ethane. The CC bond order is increased in the staggered form compared to the eclipsed form, whereas the CH bond orders are decreased. These processes are interrelated. Rehybridization at a C atom which strengthens the central bond must weaken the outer bonds. Fig. 2 shows a similar effect in hydrazine. Most important here is the split of NH bond orders, which reflects the difference between the "inner" and the "outer" pair of NH bonds. We would predict from this bond order split that there is a small difference in bond lengths between the two pairs of NH bonds. This would imply a split in the NMR signal of a spectrum. The chemical shift for the two different protons must be different. This effect would be observable only at low temperature when inversion is hindered. A discussion to this extent has been given by Dewar [13].

Finally we investigated the dependence of bond orders on bond lengths and bond angles to understand the effects of vibrations in molecules. In Figs. 3–5 we present the results for ethane. In Fig. 3 we see that there is no extremum for CC bond order



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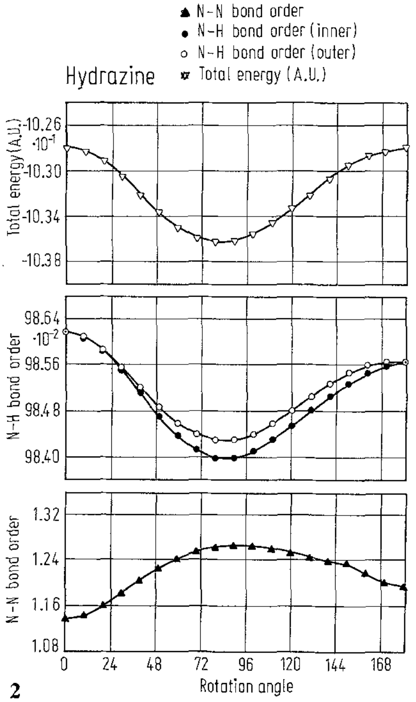

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Fig. 1. Dependence of energy and bond orders on the torsion angle in ethane

Fig. 2. Dependence of energy and bond orders on the torsion angle in hydrazine

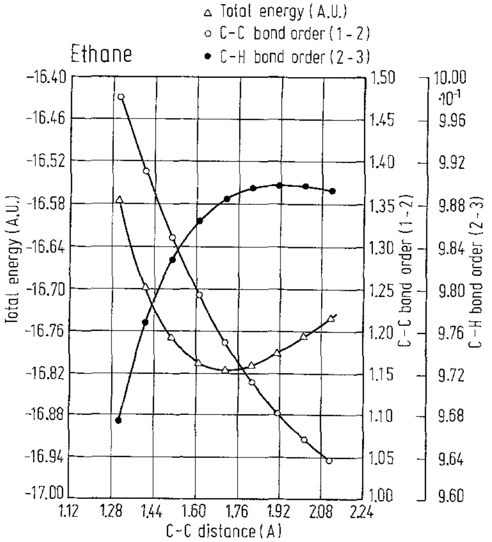

Fig. 3. Dependence of bond orders on the CC distance in ethane; C_1–C_2, H_6–H_3, H_7–H_4, H_8–H_5 are opposite to each other

at equilibrum. The CH bond orders exhibit a maximum at a CC bond length slightly increased beyond equilibrum. The increase of CC bond order with decreasing bond length is mainly due to increase in π bond character. This π bond character is usually neglected in localization procedures, but was explicitly considered by us [2]. In Fig. 4 the effect of variation of a CH bond length on all bond orders is shown. The effect is large on the CH bond involved and small on the CC bond and the other CH bonds. For the CH bond involved a decrease of bond order with increasing bond length is a consequence of the weakening of this bond. In Fig. 5 we observe that CCH bond angle changes have only a slight effect on bond orders. Similarly results are obtained in ethylene and acetylene. In allene the increase in one of the CC bond lengths is accompanied by a decrease in the related bond order and an increase in the adjacent CC bond order. The rest is similar to the effects in the other molecules. In the course of the calculations a problem showed up when very large distortions were considered. Discontinuities arose when bonding orbitals became antibonding and vice versa. This happens because the nodes of the eigenvalues of the two-center part of the density matrix and the corresponding overlap matrix are at different geometries. Since we were not considering certain dissociations where a closed shell becomes an open shell and where CI has to be invoked, these distortions were of no practical interest. However, since this discontinuity may constitute a basic problem we shall give it consideration in the future.

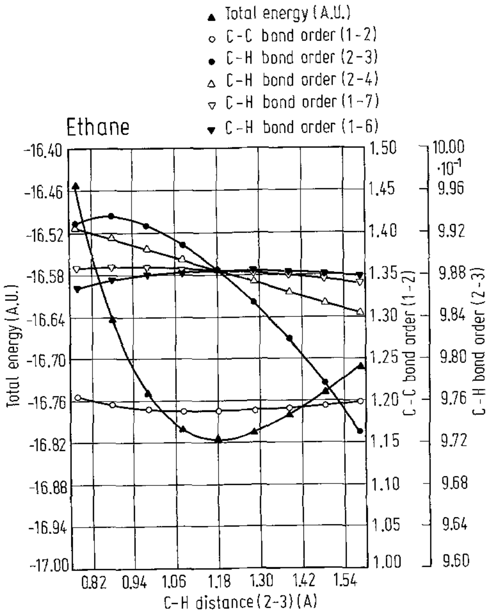

Fig. 4. Dependence of bond orders on the CH distance in ethane; labels as in Fig. 3

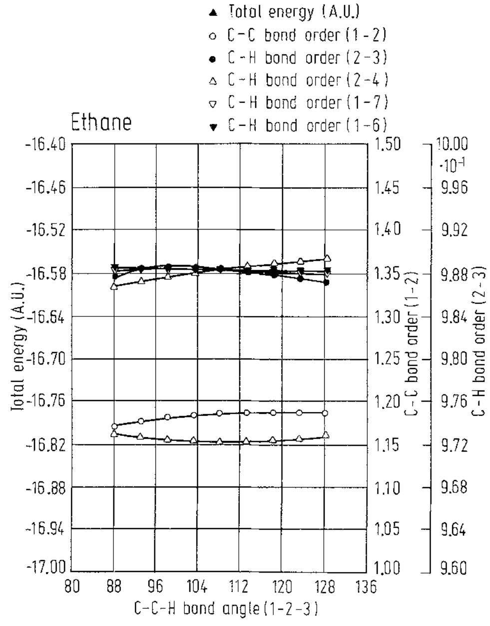

Fig. 5. Dependence of bond orders on the CCH bond angle in ethane; labels as in Fig. 3

4. Conclusion

In this work we have addressed ourselves to two principal questions. How does the newly developed maximum overlap principle compare within its various forms and to the other methods and how well does it serve in applications to measurable properties. We found that the symmetrically orthogonalized atomic basis set serves best to define the density matrix whose parts are diagonalized. We then proved that semiempirical wavefunctions are sufficient to calculate bond orders even though their optimized geometries may not be as accurate as in *ab initio* calculations. This is true when semiempirical methods generate similar wavefunctions to *ab initio* methods. Bond orders calculated with this method are similar to those by Cohen for homopolar bonds, but may be quite different in heteropolar bonds. The application to internal rotation revealed a regularity of change in bond order paralleling or opposing that one in energy. Bond lengths changes are most important for the bond order of the corresponding bond and less so for the other bonds. Bond orders do not depend strongly on bond angles. In vibrations the effect should be small because it averages out.

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