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Maximum bond order hybrid orbitals

I. Theoretical method*

Chang-Guo Zhan[1] **and Zhen-Min Hu**[1,2]

[1] Department of Chemistry, Central China Normal University, Wuhan 430070,
The People's Republic of China

[2] Department of Chemistry, Hubei Normal University, Huangshi 435002,
The People's Republic of China

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Summary. Based on the simplified calculation scheme of the maximum bond order principle and the basic idea of the maximum overlap symmetry orbital method, a simple procedure is suggested for constructing systematically the bonding hybrid orbitals, called "maximum bond order hybrid orbitals", for a given molecule from the first-order density matrix obtained from a molecular orbital calculation. As an example, the proposed procedure is performed for some typical small molecules by use of the density matrix obtained from CNDO/2 calculation. It is shown that the bonding hybrid orbitals constructed by using the procedure are extremely close to those by using the natural hybrid orbital procedure and in good agreement with chemical intuition, and that the proposed procedure can be performed more easily than the natural hybrid orbital procedure and can give simultaneously the values of the maximum bond order for all bonds in molecules.

Key words: Hybrid orbital – Maximum bond order – Maximum bond order hybrid orbital – Maximum bond order principle – Natural hybrid orbital

1 Introduction

As a generalization of the chemist's idea of single and multiple bonds, in 1976 Jug proposed the maximum bond order principle [1]. Later, this principle has been developed further and widely applied to studying molecular structure and reactivity [2–13].

In the maximum bond order principle, the calculation of the maximum bond order is a basic step. Let $A = (|a_1\rangle|a_2\rangle \cdots |a_m\rangle)$ and $B = (|b_1\rangle|b_2\rangle \cdots |b_n\rangle)$ be orthonormal atomic orbital basis sets on atoms A and B. The corresponding two sets of orthonormal hybrid orbitals G on atom A and H on atom B are expressed in:

$$\begin{cases} G = (|g_1\rangle|g_2\rangle \cdots |g_m\rangle) = AT \\ H = (|h_1\rangle|h_2\rangle \cdots |h_n\rangle) = BU \end{cases} \tag{1}$$

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Correspondence to: C.-G. Zhan

where T and U are unitary matrices of order m and n, respectively. For the sake of simplicity, we assume $m \leqslant n$. According to the maximum bond order principle, the maximum bond order P_{AB} between atoms A and B is defined as the maximum of the trace of elements of G and H coupled through the density operator $\hat{P}_{op}$ [1]:

$$P_{AB} = \mathrm{Tr}\, M_{1g} = \mathrm{Tr}(T^{+}PU) = \text{maximum} \tag{2}$$

where $\mathrm{M}_{1g} = G^{+}\hat{P}_{op}H$, $P = A^{+}\hat{P}_{op}B$ and $\mathrm{Tr} = \sum_{i}^{\min(m,n)}$. Matrix P is the two center part of the density matrix of A and B over the basis of the orthonormal atomic orbitals [1] and can be obtained from a molecular orbital calculation. According to the original calculation procedure [1] proposed by Jug himself, the maximum bond order P_{AB} can be evaluated by diagonalizing a matrix of order $(m+n) \times (m+n)$.

Recently, based on the maximum overlap method [14–19], an alternative scheme [13] for calculating the maximum bond order has been suggested to simplify the calculation procedure. The simplified scheme can be employed to obtain the value of the maximum bond order by diagonalizing matrix PP^{+} of order $m \times m$.

We know from the previous paper [13] that matrix M_{1g} satisfying Eq. (2) has the following properties:

$$M_{1g} = (M_1 \mid 0) \tag{3}$$

$$M_1^{+} = M_1 \tag{4}$$

where M_1 is a $m \times m$ Hermitian matrix formed from the first m columns of M_{1g}, and can be expressed in:

$$M_1 = G^{+}\hat{P}_{op}H_1 = T^{+}PU_1 \tag{5}$$

where $H_1 = (|b_1\rangle|b_2\rangle \cdots |b_m\rangle)U_1 = BU_1$. Clearly, H_1 is formed from the first m columns of H and U_1 from the first m columns of U. By use of matrix M_1, the maximum bond order P_{AB} can also be expressed in:

$$P_{AB} = \mathrm{Tr}\, M_1 = \text{maximum.} \tag{6}$$

Because M_1 is a Hermitian matrix, its trace, $\mathrm{Tr}\, M_1$, is unchanged under any unitary transformation, and then the number of the concrete forms of M_1 and the number of the forms of the corresponding m pairs of bond order hybrid orbitals (BOHO's) associated with a pair of atoms are all infinite. One kind of BOHO's were discussed by Jug [2].

The main purpose of this paper is to present a systematic procedure for constructing the hybrid orbitals being in accordance with the usual chemical bonding idea, going through with the maximum bond order calculation, simultaneously. For example, in the ethane molecule, we wish to construct the four bonding hybrid orbitals of atom C bonded with three hydrogens and another carbon. Performing the maximum bond order calculation, one can obtain four pairs of BOHO's for carbon-carbon bond. But, according to the chemist's idea, of the four pairs of BOHO's only one pair is important to the C–C single bond. This requires us to select the important one pair from the four pairs.

However, the condition expressed in Eq. (6) is not enough to determine the concrete forms of BOHO's. It must be combined with other new restriction condition in order to determine the concrete forms and distinct the different types of BOHO's. In this paper, we will first probe the requirement of the symmetry properties of the bonding hybrid orbitals which can be used for construction of the localized molecular orbitals. By discussing the symmetry properties of a special type of BOHO's as well as the corresponding bond order molecular orbitals, and by discussing their contributions to the maximum bond order, the reasonable restriction condition expected will be found. Based on the restriction condition, the procedure for employing the maximum bond order calculation to construct systematically the bonding hybrid orbitals will be presented.

2 Basic principle

Let us consider an imaginary diatomic molecule which is composed of atoms A and B in a molecule. If the symmetry of the chemical environment of the imaginary diatomic molecule belongs to a point symmetry group G_{AB}, then the bonding orbitals forming the A–B bond can be regarded as the ones of the imaginary molecule associated with the group G_{AB}. Therefore, the localized molecular orbitals constructed from the bonding hybrid orbitals must form the basis vectors for the irreducible representations of the point group G_{AB}. One can take the carbon-carbon double bond in ethylene as an example, in which $G_{CC} = D_{2h}$. The localized molecular orbital associated with the σ-bond forms a basis vector for the IR a_g of group D_{2h}, and that associated with the π-bond forms a basis vector for the IR b_{2u} of group D_{2h}.

In order to obtain the bonding hybrid orbitals forming the localized molecular orbitals, let us first consider the matrix M_1 as a diagonal one, a special form of the matrix:

$$(M_1)_{ij} = \langle g_i|\hat{P}_{op}|h_j\rangle = \langle g_i|\hat{P}_{op}|h_i\rangle\,\delta_{ij}. \tag{7}$$

From Eq. (2), one can get:

$$M_{1g}M_{1g}^{+} = M_1 M_1^{+} = M_1^2 = T^{+}PUU^{+}P^{+}T.$$

Because U is a unitary matrix, $UU^{+} = I$. One can obtain:

$$M_1^2 = T^{+}PP^{+}T,$$

i.e.:

$$(PP^{+})T = TM_1^2. \tag{8}$$

It follows that when M_1 is a diagonal matrix, T must be the eigenvector matrix of PP^{+}, and M_1^2 is the corresponding eigenvalue matrix. This time, M_1 is a diagonal matrix composed of the positive square roots of the m non-zero eigenvalues of PP^{+}.

Moreover, from Eqs. (2)–(4) one can also get:

$$M_{1g}^{+} = U^{+}P^{+}T$$
$$UM_{1g}^{+} = P^{+}T$$
$$U_1 M_1 = P^{+}T$$

i.e.:

$$U_1 = P^{+}TM_1^{-1}. \tag{9}$$

Equation (9) shows that so long as the matrix T is known, the matrix U_1 can be easily worked out. Apparently, that the matrices T and U_1 are known is equivalent to that the m pairs of BOHO's, G and H_1, of A–B bond are known. From the m pairs of BOHO's, the bond order molecular orbitals of A–B bond can be obtained:

$$|\psi_i^{AB}\rangle = c_{ia}^0|g_i\rangle + c_{ib}^0|h_i\rangle \tag{10}$$

where the coefficients can be determined by use of the linearly variational method. As the bond order molecular orbitals described here are the bonding molecular orbitals, the values of c_{ia}^0 and c_{ib}^0 can be all positive if $\langle g_i|h_i\rangle > 0$.

Apparently, the forms of Eqs. (8)–(10) for constructing the localized molecular orbitals are perfectly the same as those of the Eqs. (25), (32) and (13a) presented in a former paper [18] and used for constructing the delocalized MO's, $|G_i^0\rangle$'s. This means that Eqs. (8)–(10) here can be taken as special forms of the Eqs. (25), (32) and (13a) there [18]. Therefore, the conclusions about the symmetry properties of the $|G_i^0\rangle$'s described there also hold for $|\psi_i^{AB}\rangle$ presented here. That is to say, if all atomic orbitals or all valence-shell atomic orbitals of atoms A and B are taken into account, and $\hat{P}_{op}$ is a Hermitian operator which commutes with the transformation operators corresponding to the symmetry operations of the group G_{AB}, then the bond order molecular orbitals, $|\psi_i^{AB}\rangle$'s, obtained from Eqs. (8)–(10) must form the basis vectors for the IR's of the group G_{AB}. Obviously, this is certainly established here, and therefore the BOHO's forming different types of bonds will not be mixed. But for the BOHO's associated with the same symmetry types, it is not clear whether the bonding hybrid orbitals having important contributions to the A–B bond and the non-bonding hybrid orbitals having little contributions to the A–B bond may be mixed. For example, in CH_2=CH_2 there are four bond order molecular orbitals for the C–C bond. Of them the two which form basis for the IR b_{2u} of group D_{2h} will not mix with the other two which form basis for the IR a_g. But of the two associated with a_g the one corresponding to the bonding σ may be mixed with another corresponding to the non-bonding. Similar is the mix of the two associated with b_{2u}.

From the conclusion obtained in another preceding paper [19], we know that the conditions that Tr M_1 is maximum and the M_1 is diagonal are equivalent to the requirement that the all diagonal elements of M_1 take their extremum values (optimization values). That is to say, the BOHO's obtained by use of Eqs. (8) and (9) satisfy the requirement that $\langle g_i|\hat{P}_{op}|h_i\rangle$ $(=\sqrt{\lambda_i})$ takes its extremum value. This enables us to distinguish the bonding and non-bonding orbitals having the same symmetry properties, and get the bond order $\sqrt{\lambda_i} \approx 1$ for a two-electron occupied bonding orbital, $\sqrt{\lambda_i} \approx 0.5$ for a single-electron occupied bonding orbital and $\sqrt{\lambda_i} \approx 0$ for a non-bonding orbital. Therefore, that M_1 becomes a diagonal matrix is just the additional restriction condition which should be added to the condition expressed in Eq. (6) and can be employed to distinguish the all hybrid orbitals fully. The hybrid orbitals satisfying these conditions can be constructed by using Eqs. (8) and (9). The obtained bond order hybrid orbitals which have important contributions to the A–B bond ($\sqrt{\lambda_i} \approx 1$ or 0.5) will be called "maximum bond order hybrid orbitals" (MBOHO's).

Imitating the process for constructing the orthogonalized natural hybrid orbitals (NHO's) proposed by Foster and Weinhold [22], one can construct systematically the orthogonalized MBOHO's of all atoms in a molecule by use of the following procedure.

For anyone of the atoms in a molecule, when one construct its MBOHO's this atom is regarded as atom A and the other atoms bonded with A are regarded as B one by one. In this way, one can obtain the all MBOHO's of the atom A by using Eq. (8) repeatedly. One can expect an eigenvalue $\lambda_i \approx 1$ for each double-occupied covalent bond between A and B by diagonalizing the $m \times m$ matrix PP^+, and an eigenvalue $\lambda_i \approx 0.25$ (i.e. $\sqrt{\lambda_i} \approx 0.5$) for each typical single-occupied covalent bond. Several eigenvalues $\lambda_i \approx 1$ or 0.25 (i.e. $\sqrt{\lambda_i} \approx 1$ or 0.5) will be found for the multiple bond between A and B. Correspondingly, the MBOHO's of atom B bonded with atom A can be easily obtained by use of Eq. (9). By use of this process, one can find the MBOHO's for each central atom in a molecule. Since the MBOHO's found in this manner are generally non-orthogonal, it is necessary to symmetrically orthogonalize the initial MBOHO's by using the Löwdin orthogonalization process [23] in order to obtain the final orthogonalized MBOHO's for each central atom. Such an orthogonalization process has been adopted in the orthogonalization of the NHO's by Foster and Weinhold [22].

3 Numerical results and discussion

Following the procedure described in Sect. 2, we have calculated the maximum bond order hybrid orbitals for a variety of molecules, making use of the CNDO/2 approximation [24] to obtain the density matrix in each case. In the CNDO/2 approximation, only the valence-shell orbitals are considered. In the calculations, the experimental bond lengths and angles used by Sutton [25] have been employed for the molecules, and the standard geometries have been used for the others [24]. The geometries of some molecules are shown in Fig. 1.

To examine whether the MBOHO procedure is reasonable, as examples, a number of molecules have been investigated. Part of the numerical results for some typical molecules are presented in Table 1. From Table 1 it can be seen that the square roots of the eigenvalues, $\sqrt{\lambda_i}$, corresponding to the carbon-carbon bonding orbitals in ethylene are 0.9999 and 1, while the other two $\sqrt{\lambda_i}$ values are close to zero (0.0520 and 0.2431) and corresponding to the non-bonding orbitals. Also, the three $\sqrt{\lambda_i}$ values corresponding to the carbon-carbon bonding orbitals for acetylene are 0.9954, 1 and 1, and another $\sqrt{\lambda_i}$ value is 0.0825 and corresponds to the non-bonding orbital. The bonding orbitals of the carbon atom bonded with hydrogen in all cases give only one $\sqrt{\lambda_i}$ value being close to one. Moreover, the $\sqrt{\lambda_i}$ value of the vertical plane B–H bond in B_2H_6 is 0.9902, corresponding to a typical double-occupied bond, while that of the horizontal plane B–H bond is 0.6937 which is close to 0.5 and is larger than that of a typical single-occupied bond. All these results show that the conclusion, that the $\sqrt{\lambda_i}$ values corresponding to the bonding orbitals are close to 1 or 0.5 and those to non-bonding orbitals are close to zero, described in Sect. 2 is quite correct.

Another test of the MBOHO method has been performed for comparison with the NHO method. By using the procedure proposed by Foster and Weinhold [22], we have calculated the NHO's for the molecules listed in Table 2, making use of the CNDO/2 approximation [24]. The results are also listed in Table 2. It is of note that the bonding hybrid orbitals obtained by the two methods are extremely close to each other in each case. In the NHO procedure, a two-center density matrix [22] $\bar{P}^{(AB)}$ depleted of any lone-pair eigenvector must be diagonalized, while in the MBOHO procedure, the bonding hybrid orbitals can be obtained more easily. Besides, the maximum bond order can also be obtained simultaneously while the MBOHO's are constructed. But the MBOHO procedure cannot give the non-bonding hybrid orbitals.

Table 1. Eigenvalues and maximum bond order hybrid orbitals (MBOHO's) for some typical small molecules

Molecule	Bond	Square root of eigenvalue				MBOHO			Ref.
		$\sqrt{\lambda_1}$	$\sqrt{\lambda_2}$	$\sqrt{\lambda_3}$	$\sqrt{\lambda_4}$	Bond	Center	(%*p*)	Geom.
CH_3–CH_3	C–C	0.0265	0.1718	0.1718	0.9993	CC(σ)	C	72.75	25
	C–H	0.0000	0.0000	0.0000	0.9892	CH(σ)	C	75.74	
CH_3F	C–F	0.0100	0.1407	0.1407	0.9721	CF(σ)	C	80.89	25
	C–H	0.0000	0.0000	0.0000	0.9919	CH(σ)	C	73.01	
CH_2=CH_2	C=C	0.0520	0.2431	0.9999	1.0000	CC(σ)	C	59.89	25
						CC(π)	C	100.00	
	C–H	0.0000	0.0000	0.0000	0.9823	CH(σ)	C	70.05	
HC≡CH	C≡C	0.0825	0.9954	1.0000	1.0000	CC(σ)	C	44.46	25
						CC(π)	C	100.00	
	C–H	0.0000	0.0000	0.0000	0.9921	CH(σ)	C	55.54	
B_2H_6(1)	$BH_{1,2}$	0.0000	0.0000	0.0000	0.9887	$BH_{1,2}$	B	69.54	25
	$BH_{3,4}$	0.0000	0.0000	0.0000	0.6925	$BH_{3,4}$	B	82.19	
B_2H_6(1)	$BH_{1,2}$	0.0000	0.0000	0.0000	0.9902	$BH_{1,2}$	B	68.95	1
	$BH_{3,4}$	0.0000	0.0000	0.0000	0.6937	$BH_{3,4}$	B	81.02	
O=C=O	C=O	0.0671	0.6768	0.6768	0.9907				25
HCOOH(8)	C=O_1	0.0510	0.2488	0.9092	0.9855	CO_1(σ)	O_1	71.75	25
							C	35.38	
						CO_1(π)	C, O	100.00	
	C–O_2	0.0400	0.2037	0.3720	0.9184	CO_2(σ)	O_2	81.25	
							C	69.31	
	C–H	0.0000	0.0000	0.0000	0.9685	CH(σ)	C	66.30	
	O_1–H	0.0000	0.0000	0.0000	0.8947	O_1H(σ)	O_1	87.17	

In addition, the values of the maximum bond order obtained here are in good agreement with those obtained by Jug [1], who employed the SINDO wave function. For the carbon-hydrogen bonds the values of the maximum bond order are close to one in the range of 0.970–1.00. The double and triple bond orders are close to two and three, respectively. These are well in accordance with the chemist's idea of single and multiple bonds.

From Table 2 one can find the MBOHO calculation results in an excellent position to illustrate Bent's rule [26] as did by Foster and Weinhold [22] in compounds of the form CH_3X. The C–H hybrid orbitals show diminished *p*-character with increasing electronegativity of the nearest bonded atom of X in the series: –CN ($sp^{2.90}$), –CH_3 ($sp^{3.12}$), –C≡CH ($sp^{3.08}$), –H ($sp^{3.0}$), –NH_2 ($sp^{2.90}$), –OCH_3 ($sp^{2.85}$), –OH ($sp^{2.85}$) and –F ($sp^{2.70}$).

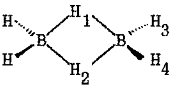
The MBOHO procedure has also been employed to analyse the hybrid orbitals of boron in diborane (B_2H_6), a special example in hydrogen-bridged compounds, taken to have the experimental geometry by Sutton [25] and the corrected geometry by Jug [1] separately (see Table 1). By using Jug's geometry,

Table 2. Comparison of maximum bond order hybrid orbitals (MBOHO's) with natural hybrid orbitals (NHO's)

No.	Molecule	Bond	Center	NHO (%p)	MBOH (%p)	P_{AB}
1	CH_4	CH(σ)	C	75.00	75.00	0.9995
2	CH_3F	CF(σ)	C	80.84	80.98	1.2635
			F	79.65	79.59	
		CH(σ)	C	73.06	73.01	0.9919
3	CH≡CH	CC(σ)	C	44.68	44.46	3.0779
		CC(π)	C	100.00	100.00	—
		CH(σ)	C	55.32	55.54	0.9921
4	CH_2=CH_2	CC(σ)	C	59.93	59.89	2.2950
		CH(π)	C	100.00	100.00	
		CH(σ)	C	70.04	70.05	0.9832
5	CH_3–CH_3	CC(σ)	C	72.70	72.75	1.3694
		CH(σ)	C	75.76	75.74	0.9892
6	Cyclopropane	CC(σ)	C	78.67	79.23	1.3731
		CH(σ)	C	71.32	70.76	0.9849
7	H_2O	OH(σ)	O	81.84	81.80	0.9897
8	NH_3	NH(σ)	N	78.95	78.99	0.9968
9	HF	HF(σ)	F	82.30	82.30	0.9728
10	HC≡N	CN(σ)	C	47.90	48.28	3.0753
			N	64.75	63.92	
		CN(π)	C, N	100.00	100.00	
		CH(σ)	C	52.10	51.73	0.9850
11	CH_3OH(2)	CO(σ)	C	78.57	78.62	1.3264
			O	78.06	77.87	
		OH(σ)	O	82.46	81.57	0.9814
		CH_1(σ)	C	74.24	74.00	0.9917
		$CH_{2,3}$(σ)	C	73.59	73.12	0.9903
12	H_2C=O	CO(σ)	C	67.27	67.40	2.3012
			O	70.71	70.52	
		CO(π)	C, O	100.00	100.00	
		CH(σ)	C	66.35	66.30	0.9755
13	CH_3NH_2(3)	CN(σ)	C	76.31	76.36	1.3517
			N	75.47	75.33	
		NH(σ)	N	79.22	78.57	0.9878
		CH_1(σ)	C	74.91	74.97	0.9893
		$CH_{2,3}$(σ)	C	74.39	74.34	0.9905
14	H_2C=C=CH_2(4)	C_1C_2(σ)	C_1	62.03	61.91	2.2919
			C_2	50.00	50.00	
		C_1C_2(π)	C_1, C_2	100.00	100.00	
		C_1H(σ)	C_1	68.99	69.04	0.9744
15	CH_3C≡N(5)	C_1C_2(σ)	C_1	72.13	72.07	1.4782
			C_2	51.46	51.47	
		C_2N(σ)	C_2	48.53	48.52	3.0126
			N	65.08	64.56	
		C_2N(π)	C_2, N	100.00	100.00	
		C_1H(σ)	C_1	75.95	75.97	0.9813

Table 2. (continued)

No.	Molecule	Bond	Center	NHO (%p)	MBOH (%p)	P_{AB}
16	CH_3OCH_3(6)	CO(σ)	C	77.99	78.19	1.3178
			O	80.33	79.23	
		CH_1(σ)	C	73.66	73.80	0.9908
		$CH_{2,3}$(σ)	C	74.17	74.01	0.9896
17	$H–C_1≡C_2–F$	C_1C_2(σ)	C_1	46.72	46.70	3.0309
			C_2	36.38	35.65	
		C_1C_2(π)	C_1, C_2	100.00	100.00	
		C_1H(σ)	C_1	53.27	53.31	0.9898
		C_2F(σ)	C_2	63.62	64.35	1.4186
			F	76.30	76.00	
18	$CH_3C≡CH$(7)	C_1C_2(σ)	C_1	44.72	44.62	3.0351
			C_2	44.78	44.44	
		C_1C_2(π)	C_1, C_2	100.00	100.00	
		C_2C_3(σ)	C_2	55.23	55.56	1.4109
			C_3	73.53	73.47	
		C_1H(σ)	C_1	55.28	55.39	0.9923
		C_3H(σ)	C_3	75.49	75.51	0.9866



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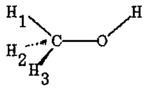

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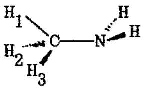

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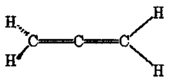

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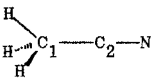

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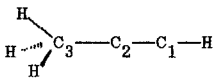

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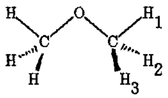

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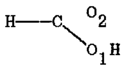

(8)

Fig. 1. Molecular geometries

the MBOHO's of the borons have 81.02% p-character ($sp^{4.27}$) and 68.95% p-character ($sp^{2.22}$) pointing at the bridging H atom and the horizontal H atom, respectively. This example illustrates the fact that the various two- and three-center electron-pair bond orbitals appear automatically in the MBOHO procedure as did in the NHO procedure.

Finally, it should be noted that the MBOHO procedure fails in conjugated molecules, such as CO_2 and benzene, as the NHO procedure did [22]. For CO_2 molecule, the MBOHO procedure gives two small $\sqrt{\lambda_i}$ values (0.6768) of carbon-oxygen π-bond (listed in Table 1), which is contrary to the unique Lewis structure. The similar results are obtained for the benzene molecule. For HCOOH molecule (see Table 1), the MBOHO calculation gives an $\sqrt{\lambda_i}$ value 0.9184, which is slightly smaller than 1, for the C–O_1 π-bond and a small $\sqrt{\lambda_i}$ value 0.3720, which is slightly bigger than 0, for the non-bonding orbital. These results would also be associated with a resonance structure, as pointed out by Foster and Weinhold [22]. However, if we only want to investigate the properties of substituents, i.e. R's in compounds of the forms R–COOH and R–C_6H_5, then the MBOHO procedure could also be performed for the atoms in R's.

4 Conclusion

A simple maximum bond order hybrid orbital procedure has been presented for constructing systematically the bonding hybrid orbitals. The procedure can be performed more easily than the NHO procedure, and can be applied (when a single resonance structure is dominant) to a variety of bonding situations. Some numerical applications for a variety of molecules have been carried out at the semi-empirical CNDO/2 level of approximate SCF-MO theory. However, it would also be applicable at any level of *ab initio* or semi-empirical theory. The resulting MBOHO's appear to be in good agreement with the NHO's determined by the NHO procedure, and the corresponding values of the maximum bond order be in good agreement with those obtained by Jug. The results obtained from the MBOHO procedure appear to be consistent with known empirical trends, such as those summarized in Bent's rule, and with the chemical intuition. In addition, the bonding hybrid orbitals obtained have been very useful in describing some chemical properties, especially those associated closely with the bonding character. The detailed numerical results will be reported in subsequent papers.

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