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Ab initio calculation of maximum bond order hybrid orbitals*

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Summary. The maximum bond order hybrid orbital (MBOHO) procedure is tested on *ab initio* level by use of the density matrix in Löwdin orthogonalized atomic orbital basis. The direct MBOHO calculation based on the whole density matrix includes also the hybridization of the inner atomic orbitals, and the MBOHO calculation based on the valence orbital part of the density matrix considers only the hybridization of the valence atomic orbitals. The concrete MBOHO calculations based on the *ab initio* calculation with STO-3G basis show that the components of the s atomic orbitals in MBOHOs and the maximum bond orders obtained from the two kinds of MBOHO calculations are very close to each other, and that the two kinds of MBOHOs all have the excellent correlativity with the nuclear spin–spin coupling constants.

Key words: Maximum bond order – Maximum bond order hybrid orbital – NMR – Nuclear spin coupling constant – *Ab initio* calculation

1 Introduction

The maximum bond order principle [1] proposed by Jug has been developed further and widely applied to studying molecular structure and reactivity [2–16]. In the maximum bond order principle, the calculation of the maximum bond order is a basic step. Recently, an alternative scheme [13] for calculating the maximum bond order has been suggested to simplify the calculation procedure. Based on this simplified scheme and the basic idea of the optimum symmetry orbitals [17–19], a simple procedure has been proposed for constructing systematically the bonding hybrid orbitals, called the maximum bond order hybrid orbitals (MBOHO's) [14], for a given molecule.

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Let $A=(|a_1\rangle|a_2\rangle\dots|a_m\rangle)$ and $B=(|b_1\rangle|b_2\rangle\dots|b_n\rangle)$ 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

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

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 $\hat{P}_{\mathrm{op}}$: [1]

$$P_{AB}=\mathrm{Tr}\,M_{1g}=\mathrm{Tr}\,M_1=\mathrm{Tr}(T^{+}\mathrm{PU})=\text{maximum} \tag{2}$$

where

$$P=A^{+}\hat{P}_{\mathrm{op}}B, \qquad \mathrm{Tr}=\sum_{\mathrm{i}}^{\min(m,n)}, \qquad M_{1g}=G^{+}\hat{P}_{\mathrm{op}}H,$$

and M_1 is a $m \times m$. Hermitian matrix formed from the first m columns of M_{1g}. According to the MBOHO method [14], the MBOHOs and the corresponding maximum bond orders can be obtained simultaneously from the diagonalization of matrix PP^{+}:

$$(PP^{+})T=TM_1^2. \tag{3}$$

Here, M_1 becomes a diagonal matrix. 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. It follows that the MBOHOs and the corresponding maximum bond orders are determined completely by the density matrix, and that the best MBOHOs and maximum bond orders should depend on *ab initio* calculation of the density matrix.

In our previous papers [14–16], the density matrix obtained from CNDO/2 calculation has been adopted to perform the MBOHO procedure, and the MBOHOs and maximum bond orders obtained have been employed to study successfully the nuclear spin–spin coupling constrants and the stretching vibrational frequencies of chemical bonds. In this short report, we attempt to perform the MBOHO procedure by use of the density matrix obtained from the *ab initio* molecular orbital calculation.

2 Calculation results and discussion

To perform the MBOHO procedure on *ab initio* level, one has to obtain a density matrix in an orthogonalized basis. Let N be the number of atomic orbitals in a molecule. The standard density matrix of order $N \times N$ in the non-orthogonalized basis for the molecule is expressed as $P(N \times N)$. The density matrix $P'(N \times N)$ in Löwdin orthogonalized basis [20] used in this work can be written as

$$P'(N \times N)=S^{1/2}P(N \times N)S^{1/2} \tag{4}$$

Because we use Löwdin orthogonalized atomic orbital basis, in *ab initio* MBOHO calculation the matrix P in Eq. (3) is formed from the sub-matrix of $P'(N \times N)$.

Table 1. Calculated coefficients of *s* orbitals in the MBOHOs and the maximum bond orders

No.	Molecule	Bond	Center	include all orbitals			valence orbitals	
				c_{1s}	c_{2s}	P_{AB}	c_{2s}	P_{AB}
1	CH_4	CH	C	0.0599	0.4964	0.9991	0.5000	0.9937
2	CH_3F	CF	C	0.0645	0.4527	1.3069	0.4567	1.3037
			F	0.0438	0.3606		0.3610	
		CH	C	0.0615	0.5098	0.9907	0.5130	0.9888
3	CHF_3	CF	C	0.0656	0.4776	1.4199	0.5039	1.4164
			F	0.0470	0.3971		0.3976	
		CH	C	0.0674	0.5686	0.9657	0.5507	0.9635
4	CH_2F_2	CF	C	0.0651	0.4642	1.3679	0.4684	1.3646
			F	0.0452	0.3767		0.3772	
		CH	C	0.0622	0.5258	0.9797	0.5298	0.9777
5	HCO(F)	CO(σ)	C	0.0645	0.5924	2.3516	0.5962	2.3476
			O	0.0560	0.5465		0.5476	
		CO(π)	C,O	0.0000	0.0000		0.0000	
		CF	C	0.0704	0.5168	1.4744	0.5211	1.4707
			F	0.0470	0.3932		0.3939	
		CH	C	0.0719	0.6065	0.9651	0.6107	0.9624
6	$CH\equiv CH$	CC(σ)	C	0.0678	0.7319	3.0631	0.7332	3.0480
		CC(π)	C	0.0000	0.0000		0.0000	
		CH	C	0.0814	0.6732	0.9958	0.6779	0.9925
7	$CH_2{=}CH_2$	CC(σ)	C	0.0661	0.6089	2.1985	0.6127	2.1925
		CC(π)	C	0.0000	0.0000		0.0000	
		CH	C	0.0670	0.5549	0.9929	0.5589	0.9907
8	CH_3CH_3	CC	C	0.0629	0.4881	1.2376	0.4920	1.2334
		CH	C	0.0598	0.4990	0.9959	0.5027	0.9940
9	Cyclopropane	CC	C	0.0556	0.4360	1.2474	0.4366	1.2439
		CH	C	0.0658	0.5561	0.9939	0.5563	0.9918
10	Cyclobutane	CC	C	0.0615	0.4800	1.1767	0.4838	1.1724
		CH	C	0.0617	0.5119	0.9935	0.5157	0.9916
11	H_2O	OH	O	0.0485	0.4376	0.9916	0.4387	0.9905
12	NH_3	NH	N	0.0545	0.4916	0.9946	0.4938	0.9932

If A and B include all atomic orbitals of atoms A and B, respectively, the matrix P is the two center part of the density matrix of A and B over the basis of all Löwdin orthogonalized atomic orbitals, then the obtained MBOHOs of atom A (or B) are linear combinations of all the atomic orbitals of atom A (or B). In this case, the hybridization includes not only the valence atomic orbitals, but also the inner atomic orbitals. However, because of the larger difference between the orbital energies of inner and valence orbitals, the components of the inner orbitals in the MBOHOs should be small. As examples, we have adopted STO-3G basis to perform the whole *ab initio* MBOHO procedure for some typical molecules. Part of the obtained results are listed in Table 1. We can see from Table 1 that the components of the inner orbitals (1*s*) in the obtained MBOHOs are the small values between 0.19% and 0.79%. If we consider only the hybridization of the valence atomic orbitals, the matrix *P* in Eq. (3) is the two center part of the density matrix of *A* and *B* over the valence orbital part of the basis of Löwdin orthogonalized atomic orbitals. The MBOHO calculation results for the valence atomic orbitals are also listed in Table 1 to compare with those for the all atomic orbitals. Table 1 reveals that the total components of the *s* atomic orbitals in the MBOHOs for the two kinds of calculations are very close to each other. That is to say,

$$c_{1s}^2(\text{all})+c_{2s}^2(\text{all})\approx c_{2s}^2(\text{valence}). \qquad (5)$$

For example, for carbon atom in methane, $c_{1s}^2(\text{all})+c_{2s}^2(\text{all})=0.0036+0.2464=0.2500$ and $c_{2s}^2(\text{valence})=0.2500$. For nitrogen atom in ammonia, $c_{1s}^2(\text{all})+c_{2s}^2(\text{all})=0.0030+0.2417=0.2447$ and $c_{2s}^2(\text{valence})=0.2438$. Correspondingly, as indicated in the table the maximum bond orders obtained from the two kinds of calculations are also very close to each other.

We have also examined the correlativity of the MBOHOs obtained from the two kinds of calculations with C–H and C–C spin-coupling constants through analysing the same molecules as those analyzed by use of MBOHO procedure under CNDO/2 approximation [15]. By applying the least-squares process for hydrocarbons with the experimental J_{CH} values appeared in the previous paper [15], we get the following good linear relationships:

$$J_{\text{CH}}=5.852[1s\%+2s\%]-19.61 \quad (R=0.9974;\ \text{SD}=3.84\ \text{Hz}) \qquad (6)$$

$$J_{\text{CH}}=5.885[2s\%\ (\text{valence})]-20.33 \quad (R=0.9975;\ \text{SD}=3.79\ \text{Hz}). \qquad (7)$$

The similar relationships have also been obtained for J_{CC} values. For the single C–C bonds with the experimental J_{CC} values appeared in the previous paper [15], we get

$$J_{\text{CC}}=3.494[1s\%+2s\%]_{\text{C1}}[1s\%+2s\%]_{\text{C2}}+13.95 \quad (R=0.9596;\ \text{SD}=2.55\ \text{Hz}) \qquad (8)$$

$$J_{\text{CC}}=3.503[2s\%(\text{valence})]_{\text{C1}}[2s\%(\text{valence})]_{\text{C2}}+13.91 \quad (R=0.9595;\ \text{S}=2.56\ \text{Hz}) \qquad (9)$$

For the multiple C–C bonds with the experimental J_{CC} values appeared in the previous paper [15] we obtain

$$J_{\text{CC}}=6.656[1s\%+2s\%]_{\text{C1}}[1s\%+2s\%]_{\text{C2}}-21.69 \quad (R=0.9985;\ \text{SD}=2.75\ \text{Hz}) \qquad (10)$$

$$J_{\text{CC}}=6.800[2s\%(\text{valence})]_{\text{C1}}[2s\%(\text{valence})]_{\text{C2}}-23.88 \quad (R=0.9984;\ \text{S}=2.83\ \text{Hz}) \qquad (11)$$

It follows that the two kinds of MBOHO calculations on the *ab initio* level are qualified for calculation of the nuclear spin–spin coupling constants, and that the results obtained from the two kinds of calculations are also very close to each other.

3 Summary and conclusion

We have tested the MBOHO procedure on *ab initio* level. The density matrix needed for MBOHO calculation is that in Löwdin orthogonalized atomic orbital basis. The direct MBOHO calculation based on the whole density matrix includes the hybridization of not only the valence atomic orbitals, but also the inner atomic orbitals. The MBOHO calculation based on the valence orbital part of the density matrix considers only the hybridization of the valence atomic orbitals. We have examined the concrete MBOHO results based on the *ab initio* calculation with STO-3G basis and can conclude that the components of the s atomic orbitals in MBOHOs and the maximum bond orders obtained from the two kinds of MBOHO calculations are very close to each other, and that the two kinds of MBOHOs all have the excellent correlativity with the nuclear spin–spin coupling constants. In order to be coincident with the ordinary idea of hybridization, we prefer to consider only the hybridization of the valence atomic orbitals in future practical application.

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