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Calculation of the maximum bond order

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Summary. Based on the maximum overlap method, an alternative scheme for the calculation of the maximum bond order defined by Jug is introduced to simplify the calculation procedure.

Key words: Bond order – Maximum bond order – Maximum bond order principle – Maximum overlap method

To describe the valence multiplicity of chemical bonds in molecules in their equilibrium and nonequilibrium situations, Jug proposed the maximum bond order principle [1] which can serve as a generalization of the chemist's idea of single and multiple bonds. This principle has since been developed further and widely applied to studying molecular structure and reactivity [2–11].

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 an orthonormal AO (atomic orbital) basis sets on atoms A and B. The corresponding two sets of orthonormal hybrids G on A and H on B are expressed as

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

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 Murrell's two theorems [12] for the maximum overlap criterion [12–16],

$$\sum_{i=1}^{m} \langle g_i|h_i\rangle = \text{maximum}, \tag{2}$$

if Eq. (2) is satisfied, then

$$\langle g_i|h_j\rangle = 0, \quad i = 1, 2, \ldots, m, \quad j = m+1, \ldots, n; \tag{3}$$

and

$$\langle g_i|h_j\rangle = \langle g_j|h_i\rangle, \quad i, j = 1, 2, \ldots, m. \tag{4}$$

Denote the $m \times n$ matrix $G^\dagger H$ by S_{1g}, $A^\dagger B$ by S, and the $m \times m$ submatrix formed from the first m columns of S_{1g} by S_1. Then Eqs. (2–4) can be expressed,

respectively,

$$\mathrm{Tr}(S_{1g}) = \mathrm{Tr}(S_1) = \mathrm{Tr}(T^{\dagger}SU) = \text{maximum}, \tag{2a}$$

$$S_{1g} = (S_1 \mid 0) \tag{3a}$$

and

$$S_1^{\dagger} = S_1. \tag{4a}$$

Apparently, Eqs. (3a) and (4a) are two necessary conditions for Eq. (2a).

Under the maximum bond order principle, the calculation of the maximum bond order is a basic step. The maximum bond order 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]:

$$P_{\mathrm{AB}} = \mathrm{Tr}\, M = \mathrm{Tr}(T^{\dagger}PU) = \text{maximum} \tag{5}$$

where $M = G^{\dagger}\hat{P}_{\mathrm{op}}H$, $P = A^{\dagger}\hat{P}_{\mathrm{op}}B$ and $\mathrm{Tr} = \sum_i^{\min(m,n)} = \sum_i^m$. Matrix P is the two center part of the density matrix of A and B over the basis of OA's [1] and can be obtained from a molecular orbital calculation. Clearly, M and P all are $m \times n$ matrices.

With a procedure [12] similar to the one that Murrell used to prove the two theorems for the maximum overlap criterion, we can prove following two necessary conditions for the requirement $\mathrm{Tr}\, M = \text{maximum}$: (1) the last $n-m$ columns of M all are zero; and (2) the submatrix M_1 formed from the first m columns of M is a $m \times m$ Hermitian matrix, i.e.

$$M = (M_1 \mid 0) \tag{6}$$

and

$$M_1^{\dagger} = M_1. \tag{7}$$

It follows that

$$MM^{\dagger} = M_1^2 = T^{\dagger}PP^{\dagger}T. \tag{8}$$

To diagonalize matrix $PP^{\dagger}$ one get

$$PP^{\dagger} = VD(\lambda_1, \lambda_2, \ldots, \lambda_m)V^{\dagger}. \tag{9}$$

Substitution of Eq. (9) into Eq. (8) gives

$$M_1^2 = (V^{\dagger}T)^{\dagger}D(\lambda_1, \lambda_2, \ldots, \lambda_m)(V^{\dagger}T)$$

$$M_1 = (V^{\dagger}T)^{\dagger}D(\pm|\sqrt{\lambda_1}|,\ \pm|\sqrt{\lambda_2}|, \ldots, \pm|\sqrt{\lambda_m}|)(V^{\dagger}T) \tag{10}$$

$$\mathrm{Tr}\, M = \mathrm{Tr}\, M_1 = \sum_{i=1}^{m} (\pm|\sqrt{\lambda_i}|). \tag{11}$$

It follows from Eqs. (9–11) that there exist 2^m forms of matrix M_1 satisfying the two necessary conditions, but only one of them satisfies the requirement $\mathrm{Tr}\, M = \text{maximum}$. If and only if all the square roots are positive values can the requirement be satisfied. Thence

$$P_{\mathrm{AB}} = \sum_{i=1}^{m} |\sqrt{\lambda_i}|, \tag{12}$$

i.e. the maximum bond order is the sum of positive square roots of eigenvalues of matrix $PP^{\dagger}$. The calculation procedure [1] of the maximum bond order is thereby simplified.

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