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Author's Review

The Maximum Overlap Principle and Optimum Symmetry Orbitals*

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This paper takes the form of a review including some original contributions. A new generalized optimization criterion, which is an extended application of the basic principle of maximum overlap, is employed to obtain a set of generalized equations for constructing various kinds of optimum orbitals. The generalized equations and the generalized conclusion obtained in this paper are useful not only for the construction of optimum symmetry orbitals, but also for direct construction of delocalized molecular orbitals and other problems. The obtained generalized conclusion on the symmetry properties of optimum orbitals shows that for a pair of bonding orbitals expressed in linear combinations of all the AOs in a molecule, so long as the criterion of maximum overlap is satisfied, the bonding orbitals must be the symmetry orbitals belonging to the same row of the same IR of the point group, *i.e.* they are symmetry-adapted. But it is uncertain whether the symmetry-adapted orbitals satisfy criterion of maximum overlap.

INTRODUCTION

In 1931, Pauling and Slater initiated the basic idea of maximum overlapping of bonding orbitals in the region between two nuclei.[1,2] Later, the principle of maximum overlap was developed. Mulliken *et al.*[3-6] examined the chemical bond strength by using the criterion of maximum overlap. Murrell was the first to propose a general maximum overlap matrix method[7] to construct systematically hybrid orbitals of the central atom in molecules of the type M-(L_1, L_2,..., L_k). Since then, this method has been applied and further developed by many others.[8-55]

Of the developed maximum overlap methods, many were used just to construct the best hybrid orbitals (HAOs) for a molecule of a known structure, but the iterative maximum overlap approximation (IMOA) method, [26,32] proposed by Maksić *et al.*, could be

* Dedicated to Professor Linus Pauling on the occasion of his 90th birthday.

applied not only to construct systematically the best HAOs but also to determine molecular geometries. The IMOA method has been employed to connect the s character of hybrid orbitals and bond overlap integrals with many physico-chemical properties, and to successfully work out the structural properties, such as bond lengths, bond angles, strain energies, heats of formation, spin-spin coupling constants across one bond, stretching frequencies, thermodynamic proton acidities and intrinsic bond energies, of a large number of molecules.[32] All these results are better than those of some semi-empirical methods and are in good agreement with the experimental data. Hybrid orbitals constructed by using the maximum overlap method have been applied not only to explain localized molecular properties, but also in a wider field, [33,34] such as rationalizing PES spectra,[35] *ab initio* calculations[36] and the PCILO method.[38,39] All these show that the basic principle of maximum overlap has played a very important role in the discussion of molecular structure and properties.

Recently, the maximum overlap method has been extended to construct the symmetry orbitals,[51-54] *i.e.* the basis vectors for irreducible representations (IRs) of the corresponding molecular point symmetry group, determined by one of the optimization criteria,[51] which can be regarded as an extension of the maximum overlap criterion. These symmetry orbitals are the optimum linear combinations of the atomic orbitals (AOs) and may be called the optimum symmetry orbitals. The optimum symmetry orbitals obtained can be used not only to block diagonalize the Hamiltonian or Fock matrix[52] but also to obtain directly a set of delocalized molecular orbitals.[51] It follows that the basic principle of maximum overlap is closely related to the symmetry properties of the bonding orbitals.

The format of this paper is primarily that of a review of the extended application of the maximum overlap principle to the construction of the optimum symmetry orbitals, but it also presents some new results concerning further extension of the method and some new insights concerning the relation between the maximum overlap and the symmetry properties of the bonding orbitals. In the following section, we will briefly discuss an important property of the maximum overlap orbitals. Based on this property, a new generalized criterion will be proposed and employed to derive a set of generalized equations for constructing various kinds of optimum orbitals in section 3. The symmetry properties and the bonding properties of the optimum orbitals will be discussed in sections 4 and 5, respectively.

OPTIMUM LINEAR COMBINATIONS OF HYBRID ORBITALS

Assuming there are m bonds in a molecule, we consider m pairs of the bonding maximum overlap hybrid orbitals forming m bonds:

$$W_1 = (|\omega_1\rangle\ |\omega_2\rangle \ldots |\omega_m\rangle)$$

$$\Psi_1 = (|\psi_1\rangle\ |\psi_2\rangle \ldots |\psi_m\rangle)$$

These hybrid orbitals satisfy the maximum overlap criterion,

$$\sum_{i=1}^{m} \langle\omega_i|\psi_i\rangle = \text{maximum}, \tag{1}$$

i.e. the sum of the m bond overlap integrals takes its maximum. Denote the overlap matrix $W_1^+\Psi_1$, by S_1. By use of matrix S_1, the condition given by Eq. (1) is equivalent to

$$\mathrm{Tr} \cdot S_1 = \text{maximum.}$$

According to Murrell's two theorems,[7] the m x m matrix S_1 must be Hermitian. It is easy to show that for each unitary matrix U,

$$U^{+}S_1U = S_1', \tag{2}$$

matrix S'_1 has the same trace as S_1, *i.e.*, if S_1 satisfies a requirement $\mathrm{Tr}\cdot S_1$ = maximum, S'_1 satisfies the condition $\mathrm{Tr}\cdot S'_1$ = maximum as well. From Eq. (2) we get

$$S'_1 = U^{+}W_1^{+}\Psi_1U = W'^{+}_1\Psi'_1 \tag{3}$$

where

$$W_1' = (|\omega'_1\rangle\ |\omega'_2\rangle \ldots |\omega'_m\rangle) = W_1U$$

$$\Psi_1' = (|\psi'_1\rangle\ |\psi'_2\rangle \ldots |\psi'_m\rangle) = \Psi_1U.$$

$|\omega'_i\rangle$s and $|\psi'_i\rangle$s are linear combinations of $|\omega_i\rangle$s and $|\psi_i\rangle$s, respectively, and satisfy also the maximum overlap criterion given by Eq. (1).

Clearly, the unitary matrix U can take an arbitrary form. However, the form will be fixed if we demand that each overlap integral $\langle\omega'_i|\psi'_i\rangle$ should take its extremum (optimum value),

$$\langle\omega'_i|\psi'_i\rangle = \text{extremum.} \tag{4}$$

Let

$$\lambda_i = \langle\omega'_i|\psi'_i\rangle = \frac{\sum_{\mu=1}^{m}\sum_{\nu=1}^{m} u^{*}_{\mu i}\, u_{\nu i}\, \langle\omega_\mu|\psi_\nu\rangle}{\sum_{j=1}^{m} u^{*}_{ji}\, u_{ji}}. \tag{5}$$

The criterion (4) can be satisfied by use of the following variational conditions:

$$\frac{\partial\lambda_i}{\partial u_{ji}} = 0, \qquad j = 1, 2, \ldots, m. \tag{6}$$

From the condition $\partial\lambda_i/\partial u_{ji} = 0$, one can get

$$S_1U_i = \lambda_iU_i \tag{7}$$

where U_i is a column matrix formed from the *i*th column of matrix U. Apparently, if we denote $|\omega'_i\rangle$, $|\psi'_i\rangle$ and S'_1 satisfying the criterion (4) by $|\omega^o_i\rangle$, $|\psi^o_i\rangle$ and S^o_1, respectively, the $|\omega^o_i\rangle = W_1U_i$, $|\psi^o_i\rangle = \Psi_1U_i$ and $(S^o_1)_{ij} = \langle\omega^o_i|\psi^o_j\rangle = \lambda_i\delta_{ij}$. Therefore, the S^o_1 matrix is a diagonal one formed from the m eigenvalues λ_is of matrix S_1, and the unitary matrix U determined by the criterion (4) is the corresponding eigenvector matrix:

$$S_1 U = U S_1^o \tag{8}$$

It follows that the overlap matrix S_1 formed from the m pairs of maximum overlap hybrid orbitals is Hermitian, but that formed from those satisfying not only the total bond overlap integral being maximum but also each overlap integral $\langle \omega_i^o | \psi_i^o \rangle$ taking its optimum value must be diagonal. In fact, if each overlap integral $\langle \omega_i^o | \psi_i^o \rangle$ takes its positive optimum value according to the optimization criterion given by Eq. (4), the total overlap integral $\Sigma_i^m \langle \omega_i^o | \psi_i^o \rangle$ must take its maximum.

It is known from a previous paper[51] that the $|\omega^o_i\rangle$s and $|\psi^o_i\rangle$s are all basis vectors for the IRs of the molecular point group. That is to say, they are the symmetry orbitals that are the optimum linear combination of the maximum overlap hybrid orbitals and are, therefore, called the optimum symmetry orbitals. Such an important conclusion will be included in the generalized conclusion presented in section 4 of the paper as a special case of $\hat{Q} = 1$ (identity operator). In addition, since the hybrid orbitals are the linear combinations of the AOs, the optimum symmetry orbitals are also the optimum linear combinations of the AOs. Practically, the optimum symmetry orbitals $|\omega^o_i\rangle$s and $|\psi^o_i\rangle$s here are just the maximum overlap symmetry orbitals (MOSOs) proposed in the previous paper.[51]

GENERALIZED EQUATIONS FOR THE CONSTRUCTION OF OPTIMUM ORBITALS

After Murrell employed the maximum overlap criterion (1) to construct the HAOs, many others have used various modified criteria of maximum overlap, such as the weighted maximum overlap criterion used in Maksić's IMOA method,[32] the criterion proposed by Lykos and Schmeising[9] and discussed by others,[10,56] the criterion of Linderberg and Öhrn's »energy weighted maximum overlap« (EWMO)[11-14] and the extended criterion for constructing the MOSOs.[51]

Here, in order to construct various kinds of optimum orbitals, we first suggest a new generalized optimization criterion, which can be regarded as an extension of the maximum overlap criterion, *i.e.*

$$\sigma_i = \frac{\langle y_i \mid \hat{Q} \mid z_i \rangle}{[\langle y_i \mid y_i \rangle \langle z_i \mid z_i \rangle]^{1/2}} = \text{optimum value.} \tag{9}$$

Let

$$Y = (|y_1\rangle \; |y_2\rangle \; \ldots \; |y_q\rangle) = (|\varphi_1\rangle \; |\varphi_2\rangle \; \ldots \; |\varphi_q\rangle) A = \Phi A$$

$$Z = (|z_1\rangle \; |z_2\rangle \; \ldots \; |z_r\rangle) = (|\chi_1\rangle \; |\chi_2\rangle \; \ldots \; |\chi_r\rangle) B = X B$$

where Φ and X are two linearly independent and normalized AO basis sets, $|y_i\rangle$s and $|z_i\rangle$s are orthonormalized optimum orbitals determined by the optimization criterion (9), and A and B are the corresponding coefficient matrices. The Hermitian operator $\hat{Q}$ in Eq. (9) may be called a generalized weighting operator, which can be the constant 1, weighting coefficient k_{AB},[26] weighting coefficient $k_{\mu\nu,P}$[51] Hamiltonian operator $\hat{H}$, Fock operator $\hat{F}$ or other Hermitian operators.

Denote matrix elements of A and B by α_{ij} and b_{ij}, respectively. We rewrite the expression of the optimum value σ_i as

$$\sigma_i = \frac{\sum_{\mu=1}^{q}\sum_{\nu=1}^{r} \alpha_{\mu i}^{*} b_{\nu i} \langle \varphi_\mu \mid \hat{Q} \mid \chi_\nu \rangle}{\left[\left(\sum_{\mu=1}^{q}\sum_{\nu=1}^{q} \alpha_{\mu i}^{*} \alpha_{\nu i} \langle \varphi_\mu \mid \varphi_\nu \rangle\right)\left(\sum_{\mu=1}^{r}\sum_{\nu=1}^{r} b_{\mu i}^{*} b_{\nu i} \langle \chi_\mu \mid \chi_\nu \rangle\right)\right]^{1/2}} \tag{10}$$

The generalized optimization criterion (9) can be expressed as the following conditions:

$$\frac{\partial \sigma_i}{\partial \alpha_{ji}} = \frac{\partial \sigma_i}{\partial b_{ki}} = 0, \qquad j = 1, 2, \ldots, q; \quad k = 1, 2, \ldots, r. \tag{11}$$

From condition $\partial\sigma_i/\partial\alpha_{ji} = 0$ and the normalization conditions of $|y_i\rangle$ and $|z_i\rangle$, one can get

$$\sum_{\nu} b_{\nu i} \langle \varphi_\mu \mid \hat{Q} \mid \chi_\nu \rangle - \sigma_i \sum_{\nu} \alpha_{\nu i} \langle \varphi_j \mid \varphi_\nu \rangle = 0$$

i.e.

$$QB_i = \sigma_i S_1 A_i \tag{12}$$

where $Q = \Phi^{+}\hat{Q}X$, $S_1 = \Phi^{+}\Phi$, and A_i and B_i are the ith columns of matrices A and B, respectively. Similarly, condition $\partial\sigma_i/\partial b_{ji} = 0$ gives

$$Q^{+}A_i = \sigma_i S_2 B_i \tag{13}$$

where $S_2 = X^{+}X$. We rewrite Eq. (13) as

$$\sigma_i B_i = S_2^{-1} Q^{+} A_i , \tag{13a}$$

and Eq. (12) as

$$Q\sigma_i B_i = \sigma_i^2 S_1 A_i . \tag{12a}$$

Substitution of Eq. (13a) into (12a) gives

$$QS_2^{-1}Q^{+}A_i = \sigma_i^2 S_1 A_i . \tag{14}$$

Similarly, one can obtain

$$Q^{+}S_1^{-1}QB_i = \sigma_i^2 S_2 B_i . \tag{15}$$

Eqs. (14) and (15) are generalized »eigenvalue equations« for the construction of optimum orbitals. When $\sigma_i \neq 0$, Eqs. (12) and (13) can also give

$$B_i = S_2^{-1} Q^{+} A_i \sigma_i^{-1} \tag{16}$$

$$A_i = S_1^{-1} Q B_i \sigma_i^{-1} . \tag{17}$$

It follows that when $\sigma_i \neq 0$, one can also employ Eq. (16) or (17) to simplify the calculation process. For convenience, let $q \geq r$. One can first use Eq. (14) to construct q $|y_i\rangle$s and then employ Eq. (16) to obtain r $|z_i\rangle$s from the first r $|y_i\rangle$s. Eqs. (14) and (16) can be, respectively, expanded as

$$QS_2^{-1}Q^+A = S_1A\Lambda \tag{14a}$$

$$B = S_2^{-1}Q^+\alpha D^{-1} \tag{16a}$$

where α is a submatrix formed from the first r columns of A, and the diagonal elements of diagonal matrices D and A are σ_1, σ_2, ...,σ_r and $\sigma^2{}_1$, $\sigma^2{}_2$, ..., $\sigma^2{}_r$, 0, 0,...,0, respectively. For convenience, we still denote the last (q – r) zero diagonal elements of Λ by $\sigma^2{}_i$ (i=r+1, r+2, ...,q). In order to solve Eq. (14a), we rewrite it as

$$(S_1^{-1/2}QS_2^{-1}Q^+S_1^{-1/2})\,(S_1^{1/2}A) = (S_1^{1/2}A)\,\Lambda\,. \tag{14b}$$

It follows that Λ is an eigenvalue matrix of $S_1^{-1/2}QS_2^{-1}Q^+S_1^{-1/2}$. If Φ and X are all orthonormal basis sets, then S_1 and S_2 are all unit matrices.

As examples, we give the following concrete forms of Eqs. (14a) and (16a):

(1). If $\hat{Q} = 1$, $Q = \Phi^+X = S$ and $\sigma_i = \langle y_i|z_i\rangle = \langle \omega^o{}_i|\psi^o{}_i\rangle$, then Eqs. (14a) and (16a) become

$$SS_2^{-1}S^+A = S_1A\Lambda \tag{14a-1}$$

$$B = S_2^{-1}S^+\alpha D^{-1}\,. \tag{16a-1}$$

These are the equations for constructing orthogonalized maximum overlap symmetry orbitals.

(2). If $\hat{Q} = \hat{H}$, $Q = \Phi^+\hat{H}X = M$ and $\sigma_i = \langle y_i|\hat{H}|z_i\rangle = \langle \omega^o{}_i|\hat{H}|\psi^o{}_i\rangle$, then Eqs. (14a) and (16a) become

$$MS_2^{-1}M^+A = S_1A\Lambda \tag{14a-2}$$

$$B = S_2^{-1}M^+\alpha D^{-1}\,. \tag{16a-2}$$

These are generalized equations for constructing the maximum overlap symmetry orbitals.[51]

(3). If $\hat{Q}$ is the density operator $\hat{P}_{op}$ employed by Jug,[57] $Q = \Phi^+\hat{P}_{op}X = P$ and $\sigma_i = \langle y_i|\hat{P}_{op}|z_i\rangle = \langle g_i|\hat{P}_{op}|h_i\rangle$, then Eq. (14a) becomes

$$PS_2^{-1}P^+A = S_1A\Lambda \tag{14a-3}$$

$$B = S_2^{-1}P^+\alpha D^{-1} \tag{16a-3}$$

Eq. (14a-3) is a generalized equation for calculating the maximum bond order.[57,50] By solving Eq. (14a-3), one can easily evaluate the maximum bond order $P_{AB} = \Sigma_i|\sigma_i|$.

(4). If $\hat{Q}$ is the delocalization energy operator, Q is the delocalization energy matrix,[58] the equation for studying the interaction of the frontier orbitals proposed by Fukui *et al.*.[58] can be regarded as a simplified form of Eq. (14a) if Φ and X are the orthonormalized, occupied and unoccupied, MO basis sets of two molecules, respectively.

(5). If $\Phi = X$ and $\hat{Q} = \hat{\delta}_{ij}$ such that $\langle \chi_i | \hat{\delta}_{ij} | \chi_j \rangle = \delta_{ij}$, $S_1 = S_2 = S$ and Q becomes a unit matrix I, then Eq. (14a) becomes

$$S^{-1}A = SA\Lambda$$

$$S^2A = A\Lambda^{-1}$$

or

$$SA = AD^{-1} \tag{14a-4}$$

which is the equation for constructing the maximum overlap atomic and molecular orbitals proposed by Lykos and Schmeising.[9] The significance of Eq. (14a-4) will be discussed deeply in a subsequent paper.

(6). If $\Phi = X$ and $\hat{Q} = 1 - \hat{\delta}_{ij}$, $S_2 = S_1 = S$, then Eq. (14a) becomes

$$(S-I)S^{-1}(S-I)A = SA\Lambda$$

or

$$(S-I)A = SAD \tag{14a-5}$$

which is the basic equation for proposing the maximum overlap population principle.[55] In Eq. (14a-5),

$$\sigma_i = 2\sum_{\mu<}\sum_{\nu} \alpha^*_{\mu i}\,\alpha_{\nu i}\,\langle \varphi_\mu | \varphi_\nu \rangle = 2\sum_{\mu<}\sum_{\nu} P^{(i)}_{\mu\nu}$$

where $P^{(i)}_{\mu\nu}$ is the overlap population between μth and νth AOs with one electron occupying the ith maximum overlap population orbital[52] if Φ is an AO basis set.

SYMMETRY PROPERTIES OF OPTIMUM ORBITALS

Eq. (14a) can be rewritten as

$$(\Phi^+\Phi)^{-1}\,(\Phi^+\hat{Q}X)\,(X^+X)^{-1}(X^+\hat{Q}^+\Phi)\,A = A\Lambda$$

$$\Phi(\Phi^+\Phi)^{-1}\,\Phi^+\hat{Q}X\,(X^+X)^{-1}X^+\hat{Q}^+Y = Y\Lambda \tag{18}$$

or

$$\hat{E}Y = Y\Lambda \tag{18a}$$

where operator $\hat{E} = \Phi(\Phi^+\Phi)^{-1}\Phi^+\hat{Q}X(X^+X)^{-1}X^+\hat{Q}^+$. It follows that $|y_i\rangle$s are eigenvectors of operator $\hat{E}$.

Furthermore, let G be a point symmetry group which has g operators as its elements:

$$G = \{\hat{O}_R\}$$

The operator $\hat{O}_R\hat{E}$ can be expressed as

$$\hat{O}_R\hat{E} = \hat{O}_R\Phi\,(\Phi^+\hat{O}_{\bar{R}}^{-1}\hat{O}_R\Phi)^{-1}\Phi^+\hat{O}_{\bar{R}}^{-1}\hat{O}_R\hat{Q}\hat{O}_{\bar{R}}^{-1}\hat{O}_R X\,(X^+\hat{O}_{\bar{R}}^{-1}\hat{O}_R X)^{-1}\,X^+\hat{O}_{\bar{R}}^{-1}\hat{O}_R\hat{Q}^+\hat{O}_{\bar{R}}^{-1}\hat{O}_R \qquad (19)$$

If $\hat{Q}$ is a linear Hermitian operator and commutes with $\hat{O}_R$, $\hat{O}_R \in G$, then Eq. (19) becomes

$$\hat{O}_R\hat{E} = (\hat{O}_R\Phi)\,[(\Phi^+\hat{O}_{\bar{R}}^{-1})\,(\hat{O}_R\Phi)]^{-1}\,(\Phi^+\hat{O}_{\bar{R}}^{-1})\,\hat{Q}\,(\hat{O}_R X)\,[(X^+\hat{O}_{\bar{R}}^{-1})\,(\hat{O}_R X)]^{-1}\,(X^+\hat{O}_{\bar{R}}^{-1})\,\hat{Q}\hat{O}_R \qquad (20)$$

Moreover, if Φ and X are normalized bases for q- and r-dimensional representations of Group G, respectively, then we have

$$\begin{cases} \hat{O}_R\Phi = \Phi D_1(\hat{R}) \\ \hat{O}_R X = X D_2(\hat{R}) \end{cases} \qquad (21)$$

$$\begin{cases} \Phi^+\hat{O}_{\bar{R}}^{-1} = D_1^{-1}(\hat{R})\Phi^+ \\ X^+\hat{O}_{\bar{R}}^{-1} = D_2^{-1}(\hat{R})X^+ \end{cases} \qquad (22)$$

Substitution of Eqs. (21) and (22) into Eq. (20) gives

$$\hat{O}_R\,\hat{E} = \Phi(\Phi^+\Phi)^{-1}\,\Phi^+\hat{Q}X(X^+X)^{-1}\,X^+\hat{Q}\hat{O}_R\ ,$$

i.e.

$$\hat{O}_R\,\hat{E} = \hat{E}\hat{Q}_R\ . \qquad (23)$$

Therefore, operator $\hat{E}$ commutes with $\hat{O}_R$, $\hat{O}_R \in G$. One can obtain from Eqs. (18a) and (23) that

$$\hat{E}(\hat{O}_R Y) = (\hat{O}_R Y)\Lambda\ . \qquad (24)$$

It follows that the eigenvectors $|y_i\rangle$s associated with the same eigenvalue of operator $\hat{E}$ form a basis for a representation of G. Similarly, it can be proved that under the same condition, $|z_i\rangle$s also form basis vectors for representations of G. In addition, one can also show that the $|z_i\rangle$ obtained by using Eq. (16a) has the same transformation properties as the $|y_i\rangle$ under all the $\hat{O}_{RS}$. A similar conclusion has been obtained in a preceding paper.[54]

For convenience, we will call optimum orbitals that all »two-orbital« integrals, *i.e.* $\langle\varphi_i|\hat{Q}|\chi_i\rangle$s, $\langle\varphi_i|\chi_i\rangle$s, $\langle\varphi_i|\varphi_i\rangle$s and $\langle\chi_i|\chi_i\rangle$s, have no contributions to the optimum values σ_is as non-bonding optimum orbitals, and the other optimum orbitals as bonding optimum orbitals. For examples, if $q \neq r$, then the optimum values for the last $(q - r)$ $|y_i\rangle$s are all zero and, therefore, the $(q - r)$ $|y_i\rangle$s are non-bonding optimum orbitals; if $X = \Phi$ and $\hat{Q} = 1 - \hat{\delta}_{ij}$, then the optimum orbitals corresponding to the zero optimum value are non-bonding optimum orbitals; if $X = \Phi$ and $\hat{Q} = \hat{\delta}_{ij}$, then the optimum orbitals corresponding to $\sigma_i = 1$ are non-bonding optimum orbitals.

Generally, if the energy of an optimum orbital $|y_i\rangle$ or $|z_i\rangle$ or an orbital obtained from a linear combination of them can be determined by the value of σ_i, then the representations associated with the bonding optimum orbitals are irreducible. Represen-

tation with respect to non-bonding optimum orbitals may be reducible and should be further reduced. A reducible representation can be reduced by finding proper optimum linear combinations of the original non-bonding optimum orbitals according to a new optimization criterion. The new optimum orbitals obtained are also symmetry orbitals. As a matter of fact, there have been some examples[51,52] supporting this conclusion.

All these symmetry orbitals determined by optimum linear combinations are called optimum symmetry orbitals. The optimum symmetry orbitals form not only the basis vectors for the IRs of group G but also satisfy an optimization criterion. Because the ordinary symmetry orbitals are only basis vectors for the IRs of the group, each of the optimum symmetry orbitals can also be regarded as an optimum linear combination of the ordinary symmetry orbitals corresponding to the same IRs. Based on this conclusion and Eqs. (14a-3) and (16a-3), a new very simple method will be proposed in a future paper[59] for obtaining systematically hybrid orbitals, which will be called »maximum bond order hybrid orbitals«, from the density matrix calculated by a molecular orbital calculation.

MOLECULAR ORBITALS FROM THE OPTIMUM SYMMETRY ORBITALS

As it is well known, the optimum symmetry orbitals have not only the symmetry properties of ordinary symmetry orbitals but also a more useful property, *i.e.* satisfying an optimization criterion. Therefore, the optimum symmetry orbitals can be used not only for the block diagonalizing of the Hamiltonian or Fock matrix and simplifying the ordinary molecular orbital calculation process, but also for other purposes. As an example in this section we present the application of a particular property to direct construction of delocalized molecular orbitals.

First of all, the atoms in a molecule are partitioned into two sets according to the condition[51] that the directly bonded atoms are partitioned into different sets, and the corresponding AOs are also partitioned into two sets Φ and X. When $\hat{Q} = \hat{H}$ and the Wolfsberg-Helmholz approximation[60] is employed, the operator $\hat{Q}$ in the optimization criterion (9) becomes a weighting coefficient $k_{\mu\nu}$ appearing in a weighted criterion of maximum overlap.[51] This time, the optimum symmetry orbitals are the maximum overlap symmetry orbitals $|\omega^o_i\rangle$s and $|\psi^o_i\rangle$ s, and can be constructed by using Eqs. (14a-2) and (16a-2). From the paper[51] in which the basic idea of the MOSOs was first proposed, we can see that if $|\omega^o_i\rangle$ and $|\omega^o_j\rangle$ $(i \neq j)$ form the basis vectors for different IRs or correspond to the different rows of the same IR of the group, we have

$$\langle \omega^o_i \mid \hat{H} \mid \omega^o_j \rangle = \langle \psi^o_i \mid \hat{H} \mid \psi^o_j \rangle = \langle \omega^o_i \mid \hat{H} \mid \psi^o_j \rangle = \langle \psi^o_i \mid \hat{H} \mid \omega^o_j \rangle$$

$$= \langle \omega^o_i \mid \omega^o_j \rangle = \langle \psi^o_i \mid \psi^o_j \rangle = \langle \omega^o_i \mid \psi^o_j \rangle = \langle \psi^o_i \mid \omega^o_j \rangle = 0 \qquad (25)$$

even if $|\omega^o_i\rangle$ and $|\omega^o_j\rangle$ $(i \neq j)$ form the basis vectors corresponding to the same row of the same IR of the group, we also have

$$\langle \omega^o_i \mid \hat{H} \mid \psi^o_j \rangle = \langle \psi^o_i \mid \hat{H} \mid \omega^o_j \rangle = \langle \omega^o_i \mid \omega^o_j \rangle = \langle \psi^o_i \mid \psi^o_j \rangle = 0\,, \qquad (26)$$

and

$$\begin{cases} \langle \omega_i^o \mid \hat{H} \mid \omega_j^o \rangle \approx 0 \\ \langle \psi_i^o \mid \hat{H} \mid \psi_j^o \rangle \approx 0 \\ \langle \omega_i^o \mid \psi_j^o \rangle \approx 0 \\ \langle \psi_i^o \mid \omega_j^o \rangle \approx 0 . \end{cases} \tag{27}$$

From Eqs. (25) - (27), one can directly get a set of delocalized molecular orbitals, $|G_i^o\rangle$s, by using the following simple linear combinations of the MOSOs:[51]

$$|G_i^o\rangle = \begin{cases} c_{ia}^o \mid \omega_i^o \rangle + c_{ib}^o \mid \psi_i^o \rangle & i = 1, 2, \ldots, r; \\ \mid \omega_i^o \rangle & i = r+1, r+2, \ldots, q. \end{cases} \tag{28}$$

For convenience, the delocalized molecular orbitals $|G_i^o\rangle$s obtained are called the maximum overlap symmetry molecular orbitals (MOSMOs). It has been shown[51] that the $|G_i^o\rangle$ obtained are close to the canonical molecular orbitals obtained by the customary LCAO method, and calculation by the MOSMO method requires less computing time than the LCAO method, thus illustrating the fact that the MOSMO method is not only a reasonable approximation of the LCAO method, but simpler and feasible in large molecular systems. This conclusion can be illustrated by listing part of the numerical results[51] in Tables I and II.

It has also been demonstrated[61] that the MOSMO method can be used for optimization of molecular geometries and calculation of vibrational frequencies by adding a two-body repulsive energy term and a modification of the Wolfsberg-Helmholz formula. The total energy of a considered molecule is expressed as a sum of two-body elec-

TABLE I

The MO energies (e.v.) for some molecules

Methane	IR	α_1	t_2(HOMO)	t_2(LUMO)	α_1	
	MOSMO	-24.530	-15.519	4.313	31.695	
	EHMO	-24.530	-15.519	4.316	31.709	
Ammonia	IR	α_1	e	α_1(HOMO)	e(LUMO)	α_1
	MOSMO	-27.419	-16.457	-14.060	2.085	18.467
	EHMO	-27.964	-16.457	-13.779	2.088	19.501
Benzene	IR	α_{1g}	e_{1u}	e_{2g}	b_{1u}	α_{1g}
	MOSMO	-28.302	-24.765	-19.488	-17.104	-16.644
	EHMO	-29.557	-25.673	-19.901	-17.149	-16.579
	IR	e_{1u}	α_{2u}	b_{2u}	e_{2g}	e_{1g}(HOMO)
	MOSMO	-14.886	-14.521	-14.295	-13.418	-12.801
	EHMO	-14.914	-14.521	-14.295	-13.376	-12.801
	IR	e_{2u}(LUMO)	b_{2g}	e_{1u}	α_{1g}	e_{2g}
	MOSMO	-8.324	-4.745	4.138	7.960	12.009
	EHMO	-8.323	-4.744	3.650	8.296	10.475
	IR	α_{1u}	α_{2g}	e_{1u}	e_{2g}	α_{1u}
	MOSMO	14.565	15.141	24.537	36.789	58.366
	EHMO	14.283	15.148	27.676	43.357	63.984

TABLE II

Running times (s) for calculating some molecules in MV/6000 computer

Molecule	Benzene (30 AOs)	$C_{18}H_{12}$ (84 AOs)	$C_{36}H_{18}$ (162 AOs)	$C_{48}H_{24}$ (216 AOs)
MOSMO	5	51	320	739
EHMO	10	122	1213	–

trostatic correction energy $E_{cor}(R)$ and the total electronic energy $E_{MOSMO}(R)$ obtained from the MOSMO calculation:

$$E(R) = E_{cor}(R) + E_{MOSMO}(R) = \sum_{\alpha<\beta} E_{\alpha\beta}(R) + \sum_{i} n_i E_i(R) \tag{29}$$

where R stands for all parameters of nuclear coordinates, $E_{\alpha\beta}(R)$ is the two-body electrostatic energy between atoms α and β, $E_i(R) = \langle G^o_i | \hat{H} | G^o_i \rangle / \langle G^o_i | G^o_i \rangle$ symbolizes the orbital energy of the ith MOSMO, and n_i the orbital occupation number. The two-body electrostatic energy $E_{\alpha\beta}(R)$ can be calculated by the following formula:[49]

$$E_{\alpha\beta}(R) = E_\beta(R) = Z_\alpha [Z_\beta R_{\alpha\beta}^{-1} - \int \rho_\beta(\vec{r}) \frac{\partial}{\partial R_{\alpha\beta}} | \vec{R}_\alpha - \vec{r} |^{-1} \, dv] \tag{30}$$

where atom β is the more electronegative atom. Some of the concrete forms of Eq. (30) can be found in literature,[62] in which the Slater orbitals have been employed. We consider only valence AOs and adopt the parametrization assumed in the EHMO method,[63] but the Wolfsberg-Helmholz formula[60] is modified as:

$$H_{ij} = 0.5 K (H_{ii} + H_{jj}) S_{ij} \exp [-L_{\alpha\beta} (R_{\alpha\beta} - d_{o\alpha\beta})] . \tag{31}$$

where $K = 1.75$ is the Wolfsberg-Helmholz constant, $R_{\alpha\beta}$ is the internuclear distance between atoms α and β to which the AO i and j belong, respectively, $d_{o\alpha\beta}$ is the standard bond length[64] of the α–β single bond, and $L_{\alpha\beta}$ is a new parameter. For example, the used $L_{\alpha\beta}$ values for several atom pairs are:

H–H:0.136; C–C:0.340; C–H:0.390; C–O:–0.090; O–H:0.228.

The obtained equilibrium geometries and vibrational frequencies are, on the whole, in good accordance with experimental data. Some of the calculation results[61] are listed in Tables III and IV.

Besides, when $X = \Phi$ is an non-orthogonal and normalized basis set composed of all the valence AOs in a molecule, we choose the operator $\hat{Q} = 1 - \hat{\delta}_{ij}$. In this case, the optimization criterion (1) becomes that given in the maximum overlap population principle:[55]

$$\sigma_i = 2 \sum_{\mu<\nu} \sum P_{\mu\nu}^{(i)} = \text{optimum value.} \tag{32}$$

TABLE III

The optimum geometries (Å, Deg) compared with the experimental data and those obtained from other methods

Molecule	MOSMO	Expt.[a]	MINDO/3[b]	MNDO[b]	CNDO/2[c]	INDO[d]	*ab initio* (HF/6-31G)
CH_4							
r(CH)	1.098	1.093		1.104		1.116	1.084
C_2H_2							
r(CH)	1.027	1.0566	1076	1.051	1.093#	1.10	1.057
r(CC)	1.198	1.2087	1.191	1.194	1.198#	1.20	1.185
C_2H_4							
r(CH)	1.066	1.086	1.098	1.089	1.110#	1.11	1.076
r(CC)	1.322	1.337	1.308	1.335	1.320#	1.31	1.317
⟨ (CCH)	122.56	121.3	124.8	123.2			121.8
CH_3CH_3							
r(CH)	1.085	1.108	1.103	1.109	1.117#	1.12	1.086
r(CC)	1.524	1.536	1.486	1.521	1.476#	1.46	1.527
⟨ (CCH)	109.15	110.1	112.8	111.2		112.2	111.19
C_6H_6							
r(CH)	1.062	1.084*	1.120	1.090			
r(CC)	1.410	1.397*	1.398	1.407			
CH_2CCH_2							
r(CH)	1.082	1.07*	1.099	1.090			
r(CC)	1.314	1.308*	1.311	1.306			
⟨ (CCH)	123.72	121.5*		122.9			
$^2CH_2$ ($^1CH_3$)$_2$							
$r(^1CH)$	1.089	1.09*					
$r(^2CH)$	1.077	1.09*					
r(CC)	1.544	1.54*					
⟨ (CCC)	111.97	111.5*					
⟨ ($^2C^1CH$)	109.15						
H_2CO							
r(CO)	1.206	1.2078			1.251#	1.25	1.184
r(CH)	1.122	1.1161			1.116#	1.12	1.092
⟨ (HCO)	118.72	121.75				115.0	122.15

[a] Experimental data with notation * come from ref. [65], those with notation ** from ref. [66], and the others from ref.]64].
[b] The MINDO/3 and MNDO calculation results come from ref. [67] and [68].
[c] The CNDO/2 calculation results with notation # come from ref. [65], and the others from ref. [64].
[d] The INDO calculation results come from ref. [64].
[e] The *ab initio* calculation results come from ref. [66], in which the data in parentheses were calculated with STO-3G basis and the others with HF/6-31G basis.

Correspondingly, the optimum symmetry orbitals become the maximum overlap population orbitals.

It has been shown[55] that the maximum overlap population orbitals determined by Eq. (14a-5) can be obtained from diagonalization of the AO overlap matrix, and can be regarded as a good approximation of the canonical molecular orbitals used for population analysis and direct calculation of the bond order, atomic valence and atomic charge.[55] The values of the bond order, atomic valence and atomic charge obtained from the maximum overlap population orbitals are in good agreement with those from the canonical molecular orbitals constructed using the *ab initio* calculation. This conclusion can be illustrated by listing part of the calculated results[55] in Table V.

TABLE IV

*The calculated vibrational frequencies (cm^{-1}), compared with the experimental data and other theoretical results**

Molecule	MOSMO	Expt.	*ab initio*	CNDO/2	INDO
H_2	4791	4160	4647	(5918)	(5918)
CO	1671	2143	2438	(3198)	(3164)
CH_4	3514	3019(t_2)	3302		
	3297	2917(a_1)	3197		
	1488	1534(e)	1703		
	1209	1306(t_2)	1488		
H_2O	3899	3756(b_1)	4188		
	3690	3657(a_1)	4070		
	1380	1595(a_1)	1826		
	3126	3009(b_1)	3231		
CH_2O	2903	2944(a_1)	3159		
	1657	1764(a_1)	2028		
	1374	1563(a_1)	1680		
	1084	1287(b_1)	1384		
	1053	1191(b_1)	1336		
C_2H_2	4198	3497(a^+g)	3719		
	3903	3415(a^+g)	3607		
	2509	2011(a^+g)	2247		
	1032	747(π_u)	883		
	894	624(π_g)	794		

*The frequencies in parentheses are evaluated by using the force constants listed in ref. [64] and the calculation formula of the harmonic vibrational frequency. The other experimental data and the *ab initio* calculation results all come from ref. [66].

TABLE V

*The bond orders, atomic valences and net atomic charges of some small molecules**

Molecule	Bond	Bond order		Atom	Atomic valence		Net atomic charge	
		Calc.	*Ab initio*[a]		Calc.	*Ab initio*	Calc.	Ab initio
H_2O	HO	0.957	0.96	O	1.915	1.92	−0.475	−0.67
				H	0.998	0.97	0.237	0.34
CH_4	CH	0.976	0.99	C	3.905	3.96	−0.525	−0.66
				H	0.998	1.00	0.131	0.17
H_2CO	CH	0.966	0.94	H	0.999	0.96	0.071	0.06
	CO	2.042	2.03	C	3.974	3.91	0.034	0.06
				O	2.105	2.11	−0.177	−0.19
CH_3OH	CO	0.988	0.87	C	3.935	3.61	−0.218	−0.27
	OH	0.961	0.82	O	1.991	1.72	−0.342	−0.68
	CH_C	0.970	0.91	H	0.998	0.83	0.237	0.37
	$CH_{C'}$	0.974	0.92	H_C	1.000	0.91	0.106	0.18
				$H_{C'}$	1.000	0.91	0.111	0.22

* All *ab initio* calculation results are based on the Mulliken population analysis.
[a] The *ab initio* calculation results of CH_3OH come from ref. [69] and the others from ref. [70].
[b] The *ab initio* calculation results come from ref. [69].

CONCLUSION

In the present paper, we have employed a generalized optimization criterion, which is an extended application of the basic principle of maximum overlapping, to obtain a set of generalized equations for constructing various kinds of optimum orbitals. If Φ and X are the bases for q- and r-dimensional representations of a group G = $\{\hat{O}_R\}$, respectively, and $\hat{Q}$ is a linear Hermitian operator which commutes with $\hat{O}_R$, then the optimum orbitals $|y_i\rangle$s and $|z_i\rangle$s associated with an optimum value σ_i all form basis for a representation of group G. In general, if the optimum values are closely related to the orbital energies, the bonding optimum orbitals are symmetry orbitals, *i.e.* the basis vectors for irreducible representations of group G. The non-bonding optimum orbitals should be further classified in order to obtain all the optimum symmetry orbitals. Such a generalized conclusion and the generalized equations obtained are useful not only for the construction of optimum symmetry orbitals, but also for the direct construction of delocalized molecular orbitals and other problems.

The conclusion for the symmetry properties of the bonding optimum orbitals shows that for a pair of bonding orbitals expressed in linear combinations of all the AOs in a molecule, so long as the criterion of maximum overlap is satisfied, the bonding orbitals must be the symmetry orbitals belonging to the same row of the same IR of the point symmetry group, *i.e.* they are symmetry-adapted. The symmetry-adapted orbitals do not, in general, satisfy the criterion of maximum overlap unless a maximization procedure has been employed to derive them. The analogy to the conventional molecular orbital theory is that molecular orbitals result from minimization of energy for a particular geometry, but symmetry adapted orbitals do not, in general, minimize the energy unless a minimization procedure has been employed.

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SAŽETAK

Načela maksimalnog prekrivanja i optimalne simetrijske orbitale

Chang-Guo Zhan

Dan je revijski prikaz metode maksimalnog prekrivanja za konstrukciju hibridnih orbitala. Autor posebice razmatra mogućnosti generalizacije i simetrijska svojstva delokaliziranih hibrida.