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Optimal group symmetric localized molecular orbitals

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Summary. The concept and generating method of optimum group symmetric localized molecular orbitals (OSLMOs) are proposed. The OSLMOs have strong points of orthogonality, equivalence and symmetry, and they are simultaneously as close to the classical VB structure as possible. By using the OSLMOs as one-electron orbitals the multiconfigurational correlation calculations are reduced. The scheme is also a valuable popularization and development to hybridization theory.

Key words: Group symmetric localized orbital – Valence bond structure – Multiconfigurational correlation – Hybridization theory – Full optimized reaction space – Optimization of orbitals

1 Introduction

The generation of localized orbitals depends on the localization criteria. There are various localization criteria [1–3]. The localized orbitals (LOs) are obtained by a unitary transformation of canonical molecular orbitals (CMOs) and are orthogonal to one another, but these methods are not directly related to molecular geometric symmetry and group theory method, and not completely in accord with the molecular symmetry and valence bond (VB) orbital due to a restriction of the orthogonal condition. We have proposed an effective algorithm generating LOs by using the coset theory method [4–6]. These LOs are called group symmetric localized molecular orbitals (SLMOs), and completely satisfy the molecular symmetry, equivalence as VB, simultaneously rigorous orthogonality as CMOs. Each SLMO can only be transformed into (up to a phase) another SLMO or itself, and no mixture of orbitals is generated under the action of any element of molecular point group G. The space symmetry adaptations of multishell electron configurations and calculations of Hamiltonian matrix elements are greatly simplified due to the use of SLMOs as configuration generating orbitals (CGOs). In this article, we develop a mathematical method from which the optimal SLMOs (OSLMOs) can be obtained and they can be applied to multiconfiguration self-consistent-field (MCSCF) iteration calculations [7, 8].

2 Fully optimized reaction space model, VB orbitals, and group symmetric LOs

The bases of atomic orbitals are classified as inner-shell and valence-shell orbitals. The inner-shell orbitals are inactive or frozen in chemical processes, and the reaction (variance) space of molecular orbitals is spanned by the full atomic valence orbitals in the molecule. According to the fully optimized reaction space (FORS) [9] model, the orbital variance space of a molecular system consists of core space, active space, and virtual space, where the occupied numbers of orbitals are 2 in core space, less than 2 in active space, and zero in virtual space. Let the sum of electrons in variation space be N, the core electron number be N_c, the active electron number be N_a, the sum of orbitals be n, the number of core orbitals be n_c, the number of active orbitals be N_a, and the number of virtual orbitals be n_v, then:

$$N = N_c + N_a, \tag{1}$$

$$n = n_c + n_a + n_v, \tag{2}$$

$$N_c = 2n_c, \quad 0 < N_a < 2n_a. \tag{3}$$

The core space contains the bonding orbitals between two atoms, the lone-pair orbitals in an atom, and three center bonds etc.. From chemical practice, the bonding rule, and capabilities of atoms in molecules it is possible to define the number of chemical bonds (containing the σ bonds, π bonds, δ bonds, or three-center bonds), long-pair electron orbitals, as well as the active electron orbitals. For molecular systems having point group symmetry the chemical bonds are classified according to inequivalent sets. For example, there are four C–H bonds in C_4H_4, 6 σ(C–C) bonds, 6 σ(C–H) bonds, 6 π(C) active orbitals in C_6H_6. Each equivalent set spans an invariant subspace by operations of the molecular point group G, and can be decomposed into one or some irreducible subspaces. Benzene (C_6H_6) belongs to group D_{6h}, where σ(C–C) is reduced to the four irrepresentations (irreps) $A_{1g}, B_{1u}, E_{1u}, E_{2g}$, σ(C–H) can be decomposed into $A_{1g}, B_{2u}, E_{1u}, E_{2g}$, π(C) into $A_{2u}, B_{1g}, E_{1g}, E_{2u}$ [4]. Therefore, each equivalent bond (or orbital, long-pair etc.) space can be characterized by its reductions into irreps. The orbitals in virtual space also can be localized in definite regions of occupied molecular orbitals. For instance, the virtual space of C_6H_6 may be decomposed into σ(C–C), σ(C–H), π(C), and spans some covariance spaces corresponding to these CGOs subspaces, respectively. Each covariance subspace in virtual space has the same symmetry and is localized in the same region with the corresponding occupied subspace in G.

The SLMOs are in one–one correspondence with the VB orbital, but the SLMOs are orthogonal, and the VB orbitals usually are nonorthogonal. The basic assumption of generating OSLMOs is that the SLMOs are as close to the real chemical bonds as possible, and simultaneously retain the orthogonal and symmetric condition.

3 The relationship between group symmetric LOs and CMOs

Let V denote the variance space, $V(t)$ denote subspace, $t = c$, a, or v denote core, active, or virtual space, respectively. Let k be smaller subspace spanned by a set of equivalent orbitals. If $t = c$, then $v(t,k)$ denotes bonding orbital space (σ, π, δ bond) or long-pair space; if $t = a$, then $v(t,k)$ denotes active orbital space; and if $t = v$, then

$v(t,k)$ represents the covariance space with a given occupied orbital space. Let $L(t,k)$ denote the dimension of $v(t,k)$.

$$v \supset v(t) \supset v(t,k) \supset v(t,k,r) \cdot f(t,k,r), \tag{4}$$

where r is the sequential number of irreps, and $r = 1, \ldots, m_r$ is the number of irreps in a molecular system; $v(t,k,r)$ is an irrep space. If $f(t,k,r) = 1$, then there is an irreducible subspace belonging to the rth irrep in $v(t,k)$. If $f(t,k,r) = 0$, then irrep r is not contained in $v(t,k)$. Therefore, $f(t,k,r)$ $(r = 1, \ldots, m_r)$ spans a vector of dimension m_r (its value of elements is 0 or 1), and is called the character information of subspace $v(t,k)$, which defines the point group symmetry of $v(t,k)$ and reduction into irreps [4].

The variance space v may be directly decomposed according to irreps:

$$v \supset v(r) \supset v(r,t) \quad (r = 1, \cdots, m_r, t = c,\ a \text{ or } v), \tag{5}$$

$$m(r) = \sum m(t,r) = m(c,r) + m(a,r) + m(v,r), \tag{6}$$

$$m(t,r) = \sum_k f(t,k,r), \tag{7}$$

$$n_t = \sum_r m(t,r) \cdot r_d, \tag{8}$$

where $v(r)$ expresses orbital variance space belonging to rth irrep, $v(r,t)$ is the subspace divided according to core, active and virtual space ($t = c$, a or v), $m(r)$ is total of irreducible subspaces in rth irrep, these $m(t,r)$ ($t = c$, a and v) are the numbers of irreducible subspaces belonging to rth irrep in core, active and virtual space, individually. r_d is the dimension of rth irrep. There exist the one, two or three dimensional irreps usually. The SLMOs and CMOs can simply be transformed by a unitary operation to each other [4].

4 Configuration correlation and LOs

The configuration correlation and electron excitation must simultaneously satisfy both conditions: the symmetric condition and neighborhood condition. Let ϕ be a configuration function, and $\phi(i \rightarrow j)$ be an excited function which expresses electron exciting from orbital i into orbital j, then: (a) i and j have the same or partly same symmetry in G; (b) if i and j are strongly localized, they must be neighborhood orbitals. Otherwise $\langle \phi | H | \phi(i \rightarrow j) \rangle \approx 0$, and the orbitals i and j are non-correlative. We define that the neighborhood orbitals are these orbitals, localized in the same or partly same region. For example, let A, B, C, D express the different atoms, where A–B and B–C are neighborhood bonds, but A–B and C–D are non-neighborhood. Both spaces containing common irreps and neighborhood orbitals are called correlation space in reference to each other. The electron of a subspace can only be excited to its correlation spaces. The numbers of common irreps in two correlation spaces is defined as their degree of correlation. The number of non-degeneracy single excited functions between two spaces are equal to their degree of correlation. For example, suppose that there are three sets of CGOs and three sets of virtual orbitals in C_6H_6 as mentioned above. The three sets of virtual orbitals may be expressed as σ(C–C)*, σ(C–H)*, π(C)*, and they are covariant with corresponding σ(C–C), σ(C–H), π(C), respectively. It is shown that these spaces are neighborhood spaces. Their degrees of correlation are shown in Table 1. The numbers of linearly independent and non-degeneracy single excited functions are listed in Table 2. If

Table 1. The degree of correlation of subspaces in C_6H_6

	$\sigma(C\text{–}C)$	$\sigma(C\text{–}H)$	$\pi(C)$
$\sigma(C\text{–}C)^*$	4	3	0
$\sigma(C\text{–}H)^*$	3	4	0
$\pi(C)^*$	0	0	4

Table 2. The linearly independent and non-degeneracy single excited wavefunctions in C_6H_6

CMOs as CGOs					
1	A_{1g}	$\sigma(C\text{–}C)\rightarrow\sigma(C\text{–}C)^*$	2	A_{1g}	$\sigma(C\text{–}C)\rightarrow\sigma(C\text{–}H)^*$
3	A_{1g}	$\sigma(C\text{–}H)\rightarrow\sigma(C\text{–}C)^*$	4	A_{1g}	$\sigma(C\text{–}H)\rightarrow\sigma(C\text{–}H)^*$
5	B_{1u}	$\sigma(C\text{–}C)\rightarrow\sigma(C\text{–}C)^*$	6	B_{2u}	$\sigma(C\text{–}H)\rightarrow\sigma(C\text{–}H)^*$
7	A_{2u}	$\pi(C)\rightarrow\pi(C)^*$	8	B_{1g}	$\pi(C)\rightarrow\pi(C)^*$
9	E_{1u}	$\sigma(C\text{–}C)\rightarrow\sigma(C\text{–}C)^*$	10	E_{1u}	$\sigma(C\text{–}C)\rightarrow\sigma(C\text{–}H)^*$
11	E_{1u}	$\sigma(C\text{–}H)\rightarrow\sigma(C\text{–}C)^*$	12	E_{1u}	$\sigma(C\text{–}H)\rightarrow\sigma(C\text{–}H)^*$
13	E_{2g}	$\sigma(C\text{–}C)\rightarrow\sigma(C\text{–}C)^*$	14	E_{2g}	$\sigma(C\text{–}C)\rightarrow\sigma(C\text{–}H)^*$
15	E_{2g}	$\sigma(C\text{–}H)\rightarrow\sigma(C\text{–}C)^*$	16	E_{2g}	$\sigma(C\text{–}H)\rightarrow\sigma(C\text{–}H)^*$
17	E_{1g}	$\pi(C)\rightarrow\pi(C)^*$	18	E_{2u}	$\pi(C)\rightarrow\pi(C)^*$
SLMOs as CGOs					
1		$\sigma(C_1\text{–}C_2)\rightarrow\sigma(C_1\text{–}C_2)^*$	2		$\sigma(C_1\text{–}C_2)\rightarrow\sigma(C_2\text{–}C_3)^*$
3		$\sigma(C_1\text{–}C_2)\rightarrow\sigma(C_3\text{–}C_4)^*$	4		$\sigma(C_1\text{–}C_2)\rightarrow\sigma(C_4\text{–}C_5)^*$
5		$\sigma(C_1\text{–}C_2)\rightarrow\sigma(C_1\text{–}H_1)^*$	6		$\sigma(C_1\text{–}C_2)\rightarrow\sigma(C_3\text{–}H_3)^*$
7		$\sigma(C_1\text{–}C_2)\rightarrow\sigma(C_5\text{–}H_5)^*$	8		$\sigma(C_1\text{–}H_1)\rightarrow\sigma(C_1\text{–}C_2)^*$
9		$\sigma(C_1\text{–}H_1)\rightarrow\sigma(C_2\text{–}C_3)^*$	10		$\sigma(C_1\text{–}H_1)\rightarrow\sigma(C_3\text{–}C_4)^*$
11		$\sigma(C_1\text{–}H_1)\rightarrow\sigma(C_1\text{–}H_1)^*$	12		$\sigma(C_1\text{–}H_1)\rightarrow\sigma(C_2\text{–}H_2)^*$
13		$\sigma(C_1\text{–}H_1)\rightarrow\sigma(C_3\text{–}H_3)^*$	14		$\sigma(C_1\text{–}H_1)\rightarrow\sigma(C_4\text{–}H_4)^*$
15		$\pi(C_1)\rightarrow\pi(C_1)^*$	16		$\pi(C_1)\rightarrow\pi(C_2)^*$
17		$\pi(C_1)\rightarrow\pi(C_3)^*$	18		$\pi(C_1)\rightarrow\pi(C_4)^*$

the CGOs are strongly localized, the electrons can only be excited between both neighborhood orbitals, and any subspace would have a few correlation subspaces. For large molecular systems, the dimension of single excited (SX) space is proportional to the number of CGOs by using strongly localized orbitals as CGOs. However, using the CMOs as CGOs, where the electron can be excited from a orbital to all of the other orbitals having the same symmetry, the dimension of SX space is proportional to the square of CGOs. Therefore, LOs have a more obvious merit to be studied in the multiconfigurational correlations than CMOs. The correlation space and degree of correlation are useful concepts in MCSCF calculations.

5 The generation of OSLMOs

Let the optimal many-electron wavefunction in MCSX space [7] obtained from the kth MCSCF iteration by ϕ, D be the first-order density matrix from ϕ. The OSLMOs (containing core, active, and virtual orbitals) using the $k+1$th iteration can be generated from the principle of maximum population.

A. It is shown that D is an Hermitian matrix and belongs to the totally symmetric representation of G. Therefore, D can be transformed into a block-diagonal form according to the component of point group irreps. Because the reduction of SLMOs into CMOs is a definite unitary transformation (see Eq. 3 in [4]), the block-diagonalization of D is simple when using SLMOs as CGOs. To solve the eigenequation in every block (the blocks for different components of an irrep are identical; therefore, in each irrep only one eigenequation is solved) and arranging CMOs in order of eigenvalue, we can classify the core, active, and virtual orbitals. The orbitals having bigger eigenvalue are core orbitals, the orbitals having smaller eigenvalue (≈ 0) are virtual orbitals. These orbitals, whose eigenvalues are between core and virtual orbitals, are active orbitals. Thus, the space of any irrep can be decomposed into three parts: the core subspace, the active subspace, and virtual subspace. Their orbitals are expressed as $c(t,r,x,y)$ ($t=c$, a and v) where x is the sequence number of orbitals in rth irrep, and y denotes the component of irrep.

B. To define projection operators

$$p_{\mathrm{ab}}=\sum_{ij}|i_{\mathrm{a}}\rangle\langle i_{\mathrm{b}}| \text{ (the bonds between both atoms a and b)}, \tag{9}$$

$$p_{\mathrm{a}}=\sum_{i}|i_{\mathrm{a}}\rangle\langle i_{\mathrm{a}}| \text{ (the orbitals in atom a)}, \tag{10}$$

$$p_{\mathrm{abc}}=\sum_{ij}(|i_{\mathrm{a}}\rangle\langle j_{\mathrm{b}}|+|i_{\mathrm{b}}\rangle\langle j_{\mathrm{c}}|+|i_{\mathrm{c}}\rangle\langle j_{\mathrm{a}}|) \text{ (the three center bond)}, \tag{11}$$

i and j sum the orbitals in an atom. To define:

$$P_{\mathrm{ab}}=\sum_{\mathrm{ab}}p_{\mathrm{ab}}, \tag{9'}$$

$$P_{\mathrm{a}}=\sum_{\mathrm{a}}p_{\mathrm{a}}, \tag{10'}$$

$$P_{\mathrm{abc}}=\sum_{\mathrm{abc}}p_{\mathrm{abc}}, \tag{11'}$$

where ab, a, abc sum the equivalent bonds, equivalent orbitals, and equivalent three-center bonds, respectively. From Eqs. (9′), (10′) (11′) it is shown that the projection operators $P_{\mathrm{ab}}, P_{\mathrm{a}}, P_{\mathrm{abc}}$ belong to the totally symmetric irrep of G. They commute with the operation g of G. Each subspace $v(t,k)$ is characterized by the corresponding projection operator $P(t,k)$. If $f(t,k,r)=1$, then $v(t,k)$ is correlative and overlapping with $v(r,t)$. To define $W(t,k,r)$ as the correlation matrix between $v(t,k)$ and $v(r,t)$, its matrix element becomes

$$W_{xx'}=(c(t,r,x,y)|P(t,k)|c(t,r,x',y)\rangle. \tag{12}$$

These elements do not relate to components y. Because the contribution of equivalent bonds to matrix elements are the same, it can be proved that

$$W_{xx'}=(L(t,k)/r_{\mathrm{d}})\sum_{y}\langle c(t,r,x,y)|p(t,k)|c(t,r,x',y)\rangle. \tag{13}$$

In solving the eigenequation, W is diagonalized. The orbital $c_1(t,r,k,y)$ called LCMO is generated, having a maximum eigenvalue in the eigenfunctions of W. Therefore, it has a maximum projection or maximum overlap with subspace $v(t,k)$, or say, localized in $v(t,k)$. For each operator $P(t,k)(\mathrm{k}=1,\ldots,L(t,k), t=c$, a or $v)$ where $f(t,k,r)=1$, we solve the eigenequation $W(t,k,r)$, and the LCMOs localized in different subspaces $v(t,k)$ can be generated. Because the number of LCMOs belonging to each component of irrep r is $m(t,r)$, the total of LCMO in space $v(r,t)$ $(t=c,\ a$ or $v)$ is $m(t,r)r_d$. These LCMOs having the same component y are nonorthogonal and linearly independent.

C. In the general case, the orthogonality and maximum projection are exclusive, and both can not be satisfied simultaneously. The VB orbitals are consistent with the maximum projection. Let us define the overlap matrix S with the matrix element:

$$S_{kx}=\langle c_1(t,r,k,y)|c(t,r,x,y)\rangle. \tag*{14)}$$

In general, the matrix S cannot be diagonalized by a unitary transformation to $c(t,r,x,y)$, but the norm of its off-diagonal elements can be substantially reduced. Since the second moment of S is invariant to such transformations, one can minimize the sum of squares of nondiagonal elements of S. Consequently, the sum of square of diagonal elements is maximized. i.e.:

$$\sum_x S_{xx}=\text{maximum} \quad x=1,\cdots,m(t,r). \tag{15}$$

The process can be performed by many 2 × 2 Jacobi rotations [10]. We define final and best orbitals through these rotations as $c_2(t,r,x,y)$. The set of $c_2(t,r,x,y)$ $(x=1,\ldots,m(t,r))$ is pressing on towards the $c_1(t,r,x,y)$ and is the optimal 'localized' and orthogonal CMOs.

D. From Eq. (3) in [4], the optimal CMOs can be transformed into OSLMOs. Thus, the OSLMOs in $k+1$th iteration are generated.

Discussion

We propose a mathematical method obtaining the OSLMOs for the $k+1$th iteration of MCSCF from the D matrix in the kth iteration. These LOs corresponding to VB orbitals are strongly localized and overlapping [11]. Simultaneously, they completely satisfy molecular geometric symmetry. Using these nonorthogonal bases, the configuration number of MCSCF and CI calculations become smaller, because the electron correlation and excitation must satisfy the symmetric condition and neighborhood condition. However, the calculations of Hamiltonian matrix elements in N-electron systems are proportional to $N!$, and are more difficult when $N>10$.

OSLMOs have the same symmetry and maximum overlapping with the corresponding VB orbital. Therefore, we can only calculate the important configurations in the process of CI and MCSCF, using the neighborhood correlation principle. Simultaneously, the calculations of matrix elements are greatly simplified due to their orthogonality. Thus, the MCSCF calculations for large molecules can be realized by using OSLMOs as CGOs.

In the FORS, multiconfigurational wavefunctions are invariant against nonsingular linear transformations among CGOs of the closed core and among active CGOs. Therefore, using OSLMOs or a nonorthogonal basis as molecular orbitals, the optimal multiconfigurational wavefunctions obtained from the variation method are completely identical. The final calculation results (as the density matrix and the electron distributions in three-dimensional space) ought to be in accordance by using nonorthogonal bases or OSLMOs. Our method as mentioned above can obtain the optimal orthogonal molecular orbitals for arbitrarily molecular systems, but the hybrid theory can only define the best orthogonal equivalent molecular orbitals of center atoms in a L_nM molecule. Therefore, OSLMOs are of wide significance as the best hybrid orbitals. It is obvious that the scheme can also be applied to solve the best hybrid orbitals.

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