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Symmetry adaptation of configuration basis in MCSCF method

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Summary. A novel approach of space symmetry adaptation is developed for multiconfigurational (MC) functions in fully optimized reaction space and complete active space SCF calculations. The bonded tableau and two box symmetric tableau are basic representations (rep) of configuration functions; the group symmetric localized orbitals are used as one-electron orbitals. The method is proposed for generating a complete and orthonormal set of MC single excited functions. The redundant variable in MCSCF can be eliminated by symmetry adaptation.

Key words: Multiconfiguration function – Complete active space – Spatial symmetry adaptation – Single excited function – MCSCF method

1 Introduction

The spatial symmetry adaptation of configuration functions [1–3] is more difficult than spin adaptation, particularly for higher symmetry point groups. A general method for point group symmetrization of configuration functions is proposed by using the group symmetric localized molecular orbitals (SLMOs) as one-electron orbitals [4–7]. We here further introduce this method for fully optimized reaction space (FORS)SCF [8, 9] and complete active space (CAS)SCF [10–13] calculations. The multiconfigurational single excited (MCSX) functions defined by Ruedenberg et al. [9] are neither normalized, mutually orthogonal, nor linearly independent. Typically the number of the effective orthogonal basis (i.e. the dimension of the SX space) is an order of magnitude lower than the number of standard SX functions. The present work proposes a method for generating the linearly independent MCSX functions which constitute a complete and orthogonal set for MCSCF calculations. The spatial symmetry adaptation can eliminate the redundant parameters in coefficient variance and orbital variance.

2 Spatial adaptation of MC functions

Based on the FORSSCF and CASSCF methods, let the sum of electrons be N, the sum of orbitals be n in orbital variance space of the molecule, the number of core orbitals be n_c, the number of core electrons be N_c, the number of active orbitals

be n_a, the number of active electrons be N_a, and the number of virtual orbitals be n_v, then

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

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

Suppose that the one-electron orbitals consist of SLMOs: $m(1, 1)$, $m(2, 1)$, ..., $m(j, i)$, ..., $m(n, d)$, where the first are core orbitals, those in the middle are active orbitals, and the latter are virtual orbitals. $m(j, i)$ expresses SLMO, j is an orbital notation, i is the notation of subspace spanned by equivalent orbitals, and d is the sum of subspaces. Let g be the group element of molecular point group G, then all $m(j, i)$ satisfy

$$gm(j, i) = \xi m(j', i), \tag{3}$$

where j and j' belong to subspace i and ξ is the phase factor. Let $n(i)$ be the dimension of the subspace, and x the sequence number of orbitals in subspace i (i_c, i_a, i_v point core, active and virtual space, respectively). $m(j, i)$ may be written as $m(j(x), i)$. The element g of G can be classified as a **coset** and written as $g(i, x, y)$; it satisfies

$$g(i, x, y)\, m(j(1), i) = \xi(x, y)\, m(j(x), i), \tag{4}$$

where $\{g(i, 1, y)\, y = 1, \ldots, y(i)\}$ spans a subgroup $G(i)$ of G; $g(i, x, 1)\,(x = 2, \ldots, n(i))$ is a coset generator; $g(i, 1, 1)$ is identity; $y(i)$ is the order of subgroup $G(i)$; and $\xi(x, y)$ is the phase factor. Suppose that occupied numbers in each active subspace are defined, i.e.,

$$N_a = \sum N(i_a), \tag{5}$$

$$0 < N(i_a) < 2n(i_a). \tag{6}$$

The subspace i can be decomposed into one or some irrepresentations (irreps) r of G. Each subspace has a character vector $\{G(i)\} = \{G_r(i),\ r = 1, \ldots, G_r)\}$, where G_r is the numbers of irreps. If subspace i contains irrep r then

$$G_r(i) = 1, \text{ otherwise } G_r(i) = 0.$$

The N-electron function space $V(n, N, S, S_z)$ is spanned by bases of spin-adapted antisymmetrized products (SAAPs) [1]. Because the core space is doubly occupied in each configuration, the dimension $f(n, N, S, S_z)$ of $V(n, N, S, S_z)$ is equal to the dimension $f(n_a, N_a, S, S_z)$ of $V(n_a, N_a, S, S_z)$ and less than the result calculated from the formula of Paldus-Weyl [1, 14] due to the restriction condition (1), (2), (5), (6).

The SAAPs are defined as

$$\Phi = A_N \Omega_0 \Theta_A, \tag{7}$$

where A_N is an antisymmetrizer and Ω_0 is a space orbital product

$$\Omega_0 = m_1(1) m_2(2) \cdots m_N(N), \tag{8}$$

and the spin function is given by

$$\begin{aligned}\Theta_A &= 2^{-1/2}[\alpha(s_1)\beta(t_1) - \alpha(t_1)\beta(s_1)] \times 2^{-1/2}[\alpha(s_2)\beta(t_2) - \alpha(t_2)\beta(s_2)] \cdots \\ &= \prod_{st}[\alpha(s)\beta(t) - \alpha(t)\beta(s)] \prod_{k} \alpha(k),\end{aligned} \tag{9}$$

where (st) extends over all pairs and k over unpaired electrons. Let R be a permutation of indices $s_1, s_2, \ldots, t_1, t_2, \ldots$:

$$\begin{aligned}\Theta_A &= R^{-1}\Theta_0 \\ &= R^{-1}2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]2^{-1/2}[\alpha(3)\beta(4) - \alpha(4)\beta(3)]\cdots,\end{aligned} \tag{10}$$

where

$$R = \begin{pmatrix} s_1 & t_1 & s_2 & t_2 \cdots \\ 1 & 2 & 3 & 4 \cdots \end{pmatrix} \tag{11}$$

obtaining a new expression for the bonded function

$$\Phi_A = A_N R^{-1}\Omega_A\Theta_0 = \varepsilon A_N\Omega_A\Theta_0, \tag{12}$$

where ε is the parity of R, and Ω_0 is replaced by Ω_A. It can be proved [15] that

$$\Phi_A = e\omega\Omega_A\varpi_A\Theta_0 \tag{15}$$

where ω and ϖ are projectors of the symmetric group which operates the orbital and spin spaces, respectively, and e is a normalization factor. The spin-independent Hamiltonian is determined by the spin-free bonded function

$$\mathrm{BT} = \mathrm{e}\omega\Omega_A, \tag{16}$$

which is called a bonded tableau (BT) [15] (a young tableu of two column). The BT an simply be represented as PQ, where P is the orbital product of the first column, and Q is the orbital product of the second column in BT.

$$\begin{aligned}P &= |m_1, m_2, \cdots, m_{(N/2+S)}|, \\ Q &= |l_1, l_2, \cdots, l_{(N/2-S)}|.\end{aligned} \tag{17}$$

Therefore, the spin-free configuration functions in $V(n, N, S, S_z)$ can be expressed by BT, a given symmetric linear combination of net space orbital products. Because n, N, S, S_z and the restriction conditions of Eqs. (1), (2), (5), (6) are definite for any configuration, the space $V(n, N, S, S_z)$ spanned by the BT can simply be written as $V(B)$. BTs (VB structure of multi-electron) are one-one correspondence with the standard young tableau of a two-column graph, in which the numbers increase from top to bottom and do not decrease from left (first column) to right (second column). But in the BT the second column can decrease from top to bottom, and each two-box describes a two-center bond or long-pair orbital. On the other hand, orbitals in the tail of a BT have parallel spins. The BT also may be expressed as a linear combination of a two-box symmetric tableau (TST's) of CAUGA (i.e. irreps of $\mathrm{U}(2^n)$) [16]. The TSTs are the eigenfunctions of S_z, but not eigenfunction of S^2. They are basis functions in $V(n, N, S_z)$. TST is represented by

$$\begin{aligned}P &= [m_1, m_2, \cdots, m_{(N/2+S)}], \\ Q &= [l_1, l_2, \cdots, l_{(N/2-S)}]\end{aligned} \tag{18}$$

or

$$\begin{aligned}P_{\mathrm{w}} &= [N^+(1), \cdots, N^+(x), \cdots, N^+(a)], \\ Q_{\mathrm{w}} &= [N^-(1), \cdots, N^-(x), \cdots, N^-(a)],\end{aligned} \tag{19}$$

where $N^+(x)$ (or $N^-(x)$) $= 1$ or 0 occurs depending upon whether the active orbital (the sequence number is x) occurs in Eq. (18) or not, a is the sum of active orbitals.

We define the net integer numbers p, q as [6, 16]

$$p = 1 + \sum_x 2^{a-x}(1 - N^+(x)),$$
$$q = 1 + \sum_x 2^{a-x}(1 - N^-(x)) \tag{20}$$

$[pq]$ or I_T express a TST, $|pq|$ or I_B express a BT, $\{pq\}$ or I express the BT or TST. We consider the value of $\{pq\}$ as smaller than $\{p'q'\}$ if $p < p'$ or if $p = p'$, then $q < q'$; thus $\{pq\}$ in V has a sequence number according to its value. BTs and TSTs can be classified according to the following principle:

1. Because the one-electron orbitals in BTs or TSTs are SLMOs, $\{pq\}$ can only be transformed into (up to a phase) another or itself and no mixture of different $\{pq\}$ is generated under the action of any element of the molecular point group G[6]. So we have

$$g\{pq\} = \xi\{p'q'\} \text{ or } gI = \xi I', \tag{21}$$

where ξ is a phase factor.

2. $\{pq\}$ is eigenvector to the number operators (E_{xx}, $x = 1, \ldots, n$) [6]:

$$E_{xx}I = W_x I, \tag{22}$$

with a set of eigenvalues (occupation numbers)

$$\{W(I)\} = \{W_x(I),\ x = 1\text{–}n\}, \tag{23}$$

which constitutes the weight $W(I)$ of I, I is said to be of higher weight than I' if $W_1(I) > W_1(I')$ or if $W_1(I) = W_1(I')$, then $W_2(I) > W_2(I')$, etc. We consider $W(I)$ and $W(I')$ as equivalent if $I' = gI$.

3. The space V is classified by K, which is a sequence number of the subspace spanned by a set of $\{pq\}$ having equivalent weight

$$V\} \quad V(K). \tag{24}$$

The highest weight in $V(K)$ is represented by $W(1, K)$. $V(K)$ is successively divided into subspaces invariant under G, and c expresses the sequence number of these subspaces:

$$V\} \quad V(K)\} \quad V(K, c), \tag{25}$$

i.e.

$$V\} \quad V(K)\} \quad V_B(K, c) \tag{26}$$

and

$$V\} \quad V(K) > V_T(K, c). \tag{27}$$

In $V(K, c)$ the I having highest weight and the least value is called the basic state and is written as $I(K, c, l)$.

4. Subspace $V(K, c)$ defines a subgroup $G(K, c)$, $g(K, c, 1, y)$ ($y = 1, \ldots, y(K, c)$) is its element, $g(K, c, 1, 1)$ is identity, $y(K, c)$ is the order of subgroup $G(K, c)$, and $g(K, c, x, 1)$ ($x = 2, \ldots, n(k, c)$) is a coset generator

$$g(K, c, x, y)I(K, c, 1) = \xi(x, y)I(K, c, x). \tag{28}$$

The subspace $V(K, c)$ can be decomposed into irrep r of G. Each subspace has a character vector $\{G(K, c)\} = \{G_r(K, c); r = 1\text{–}G_r\}$ if $V(K, c)$ contains irrep r; then

$G_r(K, c) = 1$, otherwise $G_r(K, c) = 0$.

5. Projectors of G are represented by P_{ru}, where r labels the irrep, u labels the component belonging to multidimensional irrep. Suppose:

$$S_T(K, c, r, u) = P_{ru} I_T(K, c, 1), \tag{29}$$

$$S_B(K, c, r, u) = P_{ru} I_B(K, c, 1), \tag{30}$$

or, general

$$S(K, c, r, u) = P_{ru} I(K, c, 1). \tag{31}$$

The $S(K, c, r, u)$ is a space symmetry-adapted basis if $G_r(k, c) = 1$. It is a linear combination of configuration functions in $V(K, c)$.

6. $I_T(K, c, x)$ and $S_T(K, c, r, u)$ are orthogonal sets, and $I_B(K, c, x)$ having different weight are also orthogonal to each other, but $I_B(K, c, x)$ having the same weight are nonorthogonal in the general case. $V_B(K, c)$ usually contains one or some $V_T(K, c)$. Let $n_T(V)$ be the number of $V_T(K, c)$ in V; $n_B(V)$ be the number of $V_B(K, c)$; the linearly independent I_B and $n_B(V)$ are less than corresponding I_T and $n_T(V)$, respectively. The dimension $n_B(V, r)$ of irrep r is equal to or less than $n_B(V)$. The dimension $n_T(V, r)$ of irrep r is equal to or less than $n_T(V)$:

$$V_B(K, c) = \sum V_T(K, c'), \tag{32}$$

$$I_B = \sum I_T, \tag{33}$$

$$S_B(K, c, r, u) = \sum S_T(K, c', r, u), \tag{34}$$

$$n_T(V, r) \geqslant n_B(V, r), \tag{35}$$

$$n_T(V, r) \leqslant n_T(V), \tag{36}$$

$$n_B(V, r) \leqslant n_B(V), \tag{37}$$

where $n_T(V, r)$ is the number of independent and orthogonal $S_T(K, c, r, u)$, and $n_B(V, r)$ is the number of independent and nonorthogonal $S_B(K, c, r, u)$ in irrep space $V(r)$. V is the direct sum of $V(r)$:

$$V = V(1) + \cdots + V(r) + \cdots + V(G_r). \tag{38}$$

7. Let MC( ) be an optimized MC function obtained from the variance method in $V(r)$:

$$\mathrm{MC}(r, u) = \sum_{Kc} C_B(K, c, r) S_B(K, c, r, u) = \sum_{Kc} C_T(K, c, r) S_T(K, c, r, u). \tag{39}$$

$C_B(K, c, r)$ is linearly independent, but $C_T(K, c, r)$ is linearly dependent. Between $C_T(K, c, r)$ and $C_B(K, c, r)$ there exist some restriction conditions, i.e. the coefficient $C_T(K, c, u)$, whose number is $n_T(V, r)$; only the numbers of $n_B(V, r)$ are linearly independent. MC( ) has the quantum number S, S_z, r, u, and is an optimized configuration function satisfying space symmetry, spin symmetry and the Pauli principle in MC space.

8. Suppose

$$\mathrm{MC}(r) = \sum_u \mathrm{MC}(r, u), \tag{40}$$

where $\mathrm{MC}(r)$ is invariant (up to a phase) under G.

3 Symmetrization of MCSX functions

Let $V(i_1)$ be a subspace of orbitals, and $V(i_2)$ be another subspace of orbitals. We then define the generator of the unitary group E as

$$E(x_1, i_1; x_2, i_2)\mathrm{MC}(r) = \mathrm{MC}(j_1(x_1), i_1 \to j_2(x_2), i_2) - \mathrm{MC}(j_2(x_2), i_2 \to j_1(x_1), i_1) \tag{41}$$

in Eq. (41) (1) $i_1 < i_2$; (2) i_1 belongs to the core space or active space and i_2 belongs to the active space and virtual space; (3) i_1 and i_2 are correlation space [7]. $E(x_1, i_1; x_2, i_2)$ spans an invariant subspace under G. In the subspace we define $E(1, i_1; x, i_2)$ as a basic generator and simply express the subspace as $V(i_1, x, i_2)$. Let P_1 be the projector of totally symmetric irrep in G, and define

$$E(i_1, x, i_2) = P_1 E(1, i_1, x, i_2). \tag{42}$$

Between i_1 and i_2 the number of invariant subspaces $V(i_1, x, i_2)$ (the sequence number x varies in different subspaces) is referred to as their degree of correlation [7]. If $E(i_1, x, i_2)$ acts on $\mathrm{MC}(r)$, we obtain the MCSX function $\mathrm{SX}(i_1, x, i_2)$:

$$eE(i_1, x, i_2)\mathrm{MC}(r) = SX(i_1, x, i_2), \tag{43}$$

where e is a normalization factor. If $i_1 \neq i'_1$ or i_2 i'_2, then $\mathrm{SX}(i_1, x, i_2)$ and $\mathrm{SX}(i', x, i'_2)$ are orthogonal due to different weight vectors. If $i_1 = i_1$ and $i_2 = i'_2$, then $\mathrm{SX}(i_1, x, i_2)$ and $\mathrm{SX}(i'_1, x, i'_2)$ may be nonorthogonal. But to a greater extent they are linearly independent. By using the Schmidt process [17] the complete and independent set of MCSX functions is generated. The dimension (i.e. the number of independent variant parameters) of SX space is no more than the number of all subspaces $V(i_1, x, i_2)$ in orbital variance space, and all $\mathrm{SX}(i_1, x, i_2)$ span a complete set of MCSX space

We imagine that an orbital is a point, and a pair of correlation orbitals ($m(j_1(x_1), i_1)$ and $m(j_2(x_2), i_2)$ are an edge in orbital variance space. The equivalent edge spans a subspace invariant under G, and basically generates a linearly independent single-excited SX function. The number of inequivalent edges is no less than the dimension of SX space.

4 Practical example

In order to illustrate the mathematical method mentioned above, let us consider a simplified model of the benzene molecule. Suppose that benzene (C_6H_6) has a core space σ(C–C), σ(C–H), active space π(C), and virtual space σ^*(C–C), σ^*(C–H), π^*(C) covariant with corresponding CGO space, respectively [7]. The orbital variance space has 6 subspaces and 36 orbitals. These molecular orbitals are

σ(C–C): $m(1(1), 1)$, $m(2(2), 1)$, $m(3(3), 1)$, $m(4(4), 1)$,
$m(5(5), 1)$, $m(6(6), 1)$

σ(C–H): $m(7(1), 2)$, $m(8(2), 2)$, $m(9(3), 2)$, $m(10(4), 2)$,
$m(11(5), 2)$, $m(12(6), 2)$

π(C): $m(13(1), 3)$, $m(14(2), 3)$, $m(15(3), 3)$, $m(16(4), 3)$,
$m(17(5), 3)$, $m(18(6), 3)$

Table 1. Basic BTs ($I_B(K,c,1)$) in CGO space of C_6H_6

K	c	P	Q	$W(1,K)$	K	c	P	Q	$W(1,K)$
1	1	|1,2,3|	|1,2,3|	{222000}	2	1	|1,2,3|	|1,2,4|	{221100}
3	1	|1,2,3|	|1,2,5|	{221010}	4	1	|1,2,3|	|1,2,6|	{221001}
5	1	|1,3,2|	|1,3,4|	{212100}	6	1	|1,3,2|	|1,3,5|	{212010}
7	1	|1,2,4|	|1,3,5|	{211110}	7	2	|1,2,3|	|1,5,4|	{212010}
8	1	|1,2,5|	|1,3,6|	{211011}	8	2	|1,2,3|	|1,6,5|	{211011}
9	1	|1,2,5|	|1,4,6|	{210111}	9	2	|1,2,4|	|1,6,5|	{210111}
10	1	|1,3,5|	|2,4,6|	{111111}	10	2	|1,3,4|	|2,6,5|	{111111}
11	1	|1,2,4|	|1,2,4|	{220200}	12	1	|1,2,4|	|1,2,5|	{220110}
13	1	|1,4,5|	|1,4,6|	{200211}	14	1	|1,2,4|	|1,5,4|	{210210}
15	1	|1,4,3|	|1,4,5|	{201210}	16	1	|1,5,2|	|1,5,4|	{210120}
17	1	|1,5,3|	|1,5,4|	{201120}	18	1	|1,3,5|	|1,3,5|	{202020}

σ^*(C–C): $m(19(1),4)$, $m(20(2),4)$, $m(21(3),4)$, $m(22(4),4)$, $m(23(5),4)$, $m(24(6),4)$

σ^*(C–H): $m(25(1),5)$, $m(26(2),5)$, $m(27(3),5)$, $m(28(4),5)$, $m(29(5),5)$, $m(30(6),5)$

π^*(C): $m(31(1),6)$, $m(32(2),6)$, $m(33(3),6)$, $m(34(4),6)$, $m(35(5),6)$, $m(36(6),6)$.

The configuration functions $I(I_B$ or $I_T)$ in space of CGOs may be classified according to K, c and expressed by P, Q or $\{pq\}$. Because in core space the orbitals are doubly occupied for all configurations, these core orbitals are not pointed, for example $P = \{\ldots \text{core} \ldots, m(13(1),3), m(14(2),3), m(15(3),3)\} = \{1,2,3\}$, $Q = \{\ldots \text{core} \ldots, m(16(4),3), m(17(5),3), m\{18(6),3)\} = \{4,5,6\}$ etc. The basic configuration functions $I_B(K,c,1)$ and $I_T(K,c,1)$ are listed in Tables 1 and 2 [6].

Between BTs and TSTs there are the following relations:

$$I_B(7,1,1) = |1,2,4|\,|1,3,5| = 2^{-1/2}([1,2,4][1,3,5] + [1,2,5][1,3,4])$$
$$= 2^{-1/2}([12,22] + [14,20])$$
$$I_B(7,2,1) = |1,2,3|\,|1,5,4| = -2^{-1/2}([1,2,3][1,4,5] + [1,2,4][1,3,5])$$
$$= -2^{-1/2}([8,22] + [12,22])$$
$$I_B(8,1,1) = |1,2,5|\,|1,3,6| = 2^{-1/2}([1,2,5][1,3,6] + [1,2,6][1,3,5])$$
$$= 2^{-1/2}([14,23] + [15,22])$$
$$I_B(8,2,1) = |1,2,3|\,|1,6,5| = -2^{-1/2}([1,2,3][1,5,6] + [1,2,5][1,3,6])$$
$$= -2^{-1/2}([8,29] + [14,23])$$
$$I_B(9,1,1) = |1,2,5|\,|1,4,6| = 2^{-1/2}([1,2,5][1,4,6] + [1,2,6][1,4,5])$$
$$= 2^{-1/2}([14,27] + [15,26])$$
$$I_B(9,2,1) = |1,2,4|\,|1,6,5| = -2^{-1/2}([1,2,4][1,5,6] + [1,2,5][1,4,6])$$
$$= -2^{-1/2}([12,27] + [14,27])$$

Table 2. Basic TSTs ($I_T(K,c,1)$) in CGO space of C_6H_6

K	c	P	Q	p	q	K	c	P	Q	p	q
1	1	[1,2,3]	[1,2,3]	8	8	2	1	[1,2,3]	[1,2,4]	8	12
3	1	[1,2,3]	[1,2,5]	8	14	4	1	[1,2,3]	[1,2,6]	8	13
5	1	[1,3,2]	[1,2,4]	8	12	6	1	[1,3,2]	[1,3,5]	8	22
7	1	[1,2,4]	[1,3,5]	12	22	7	2	[1,2,3]	[1,5,4]	8	26
7	3	[1,2,5]	[1,3,4]	14	20	8	1	[1,2,5]	[1,3,6]	14	23
8	2	[1,2,3]	[1,6,5]	8	29	8	3	[1,2,6]	[1,3,5]	15	22
9	1	[1,2,5]	[1,4,6]	14	27	9	2	[1,2,4]	[1,5,6]	12	29
9	3	[1,2,6]	[1,4,5]	12	29	10	1	[1,3,5]	[2,4,6]	22	43
10	2	[1,3,4]	[2,6,5]	20	45	10	3	[1,2,3]	[4,5,6]	8	57
11	1	[1,2,4]	[1,2,4]	12	12	12	1	[1,2,4]	[1,2,5]	12	14
13	1	[1,4,5]	[1,4,6]	26	27	14	1	[1,4,2]	[1,4,5]	12	26
15	1	[1,3,4]	[1,4,5]	20	26	16	1	[1,2,5]	[1,4,5]	12	26
17	1	[1,3,5]	[1,4,5]	22	26	18	1	[1,3,5]	[1,3,5]	26	26

$$
\begin{aligned}
I_B(10,1,1) &= |1,3,5|\,|2,4,6| \\
&= 2^{-1}([1,3,5][2,4,6] + [1,4,5][2,3,6]) + [1,4,6][2,3,5] \\
&\quad + [1,3,6][2,4,5]) \\
&= 2^{-1}([22,43] + [26,39] + [27,38] + [23,42]) \\
I_B(10,2,1) &= |1,3,4|\,|2,6,5| \\
&= -2^{-1}([1,3,4][2,5,6] + [1,4,6][2,3,5] \\
&\quad + [1,5,6][2,3,4] + [1,3,5][2,4,6]) \\
&= -2^{-1}([20,45] + [27,38] + [29,36] + [22,43])
\end{aligned}
$$

Let P_{ru} act on these BTs; we obtain the $S_B(K,c,r,u)$ belonging to irreps, for example

$$
\begin{aligned}
S_B(10,1,1,1) &= eP_{11}I_B(10,1,1) = eP_{11}(I_T(10,1,1) + (3/2)^{1/2} I_T(10,2,1)) \\
&= eP_{11}([22,43] + (3/2)^{1/2}[20,45]) \\
&= e_1(S_T(10,1,1,1) + (3/2)^{1/2} S_T(10,2,1,1)) \\
S_B(10,2,1,1) &= e'P_{11}I_B(10,2,1) \\
&= e'P_{11}(-I_T(10,1,1) - (2/3)^{1/2} I_T(10,2,1) - (1/3)^{1/2} I_T(10,3,1)) \\
&= e'P_{11}(-[22,43] - (2/3)^{1/2}[20,45] - (1/3)^{1/2}[8,57]) \\
&= e'_1(S_T(10,1,1,1) + (2/3)^{1/2} S_T(10,2,1,1)) + (1/3)^{1/2} S_T(10,3,1,1))
\end{aligned}
$$

where e, e_1, e', e'_1 are normalization factors. The optimized MC function belonging to totally symmetric irrep in MC space of C_6H_6 can be written as

$$\mathrm{MC}(1) = \sum_{Kc} C_T(K,c) S_T(K,c,1,1).$$

Between these coefficients $C_T(K,c)$ for $K = 7,8,9,10$ there exists a restriction condition, respectively. For example,

$$C_T(8,1) = C_T(8,2) + C_T(8,3)$$

and the normalization condition:

$$\sum_{Kc} c_T(K,c) = 1$$

Therefore, the number of independent parameters is 21 in MC space of C_6H_6.

In MCSX space, the number of linearly independent SX functions (the dimension of SX space) is 18 [7]; these functions are:

$$\mathrm{SX}(1,1,4), \mathrm{SX}(1,2,4), \mathrm{SX}(1,3,4), \mathrm{SX}(1,4,4), \mathrm{SX}(1,1,5),$$

$$\mathrm{SX}(1,3,5), \mathrm{SX}(1,4,5), \mathrm{SX}(2,1,4), \mathrm{SX}(2,2,4),$$

$$\mathrm{SX}(2,3,4), \mathrm{SX}(2,1,5), \mathrm{SX}(2,2,5), \mathrm{SX}(2,3,5), \mathrm{SX}(2,4,5),$$

$$\mathrm{SX}(3,1,6), \mathrm{SX}(3,2,6), \mathrm{SX}(3,3,6), \mathrm{SX}(3,4,6)$$

The number of coefficient variance and orbital variance parameters in MCSCF is greatly reduced by spatial symmetry adaptation.

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