On geminals and symplectic bases in quantum chemistry

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The construction of a symplectic basis set with N electrons is exhibited by means of three kinds of units, the first kind geminal, the second kind geminal and the one-particle operators. The optimization procedure of the variation method is extended to the coefficients in the linear sum of the symplectic bases, the parameters in the geminals, and the orbitals. For practical use, these bases are expanded explicitly as a linear sum of the Slater determinants. For illustration, the LiH molecule, which is taken as an example, is calculated by using some symplectic bases.

1. Introduction

The projected BCS or pairing function – or, as we prefer, the antisymmetrized geminal power function (AGP) – has appeared in several places in physics and chemistry. It is now widely admitted [1] that the chief cornerstone of the BCS theory of superconductivity is the assumption that the wave function is AGP. It is also the ground state of the B-condition for N-representability [2–4]. Recently, it was recognized that the AGP function is an appropriate ground state for permitting the Random Phase Approximation to be self-consistent. This appreciation led to renewed successful applications of AGP and GAGP to the chemistry of molecules [5,8,10–13,16–19,21–25]. A suggestion of Mottelson in 1959 has led to a pairing "industry" in nuclear physics exploiting the AGP function. Reference [5] gives an entry into this large literature.

The object of the present paper is to exhibit the construction of $\binom{2M}{N}$ N-electron bases with symplectic symmetry by means of three kinds of units, the first kind geminal, the second kind geminal, and the one-particle operators. These bases contain AGP which acts as an important one in the computation of ground state for even N. The idea of invoking the symplectic group to obtain "good" quantum numbers to specify a wave function goes back at least to Flower in 1952 [7,9]. In this paper, a modified branching rules of symplectic group in equations (40) and (41) which play a crucial role are introduced instead of the symplectic diagram technique in the previous paper [28]. The types of the symplectic bases for even N are classified as AGP (Antisymmetrized Geminal Power), SPG (Sequential Product of Geminals), AGP-SPG, GAGP (Generalized AGP), GSPG (Generalized SPG), G(AGP-SPG) (Generalized AGP-SPG) and SD (Slater Determinant), whereas for odd N, no types like AGP, SPG and AGP-

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SPG appear in the bases. Furthermore, the symplectic bases are expanded explicitly as the linear sum of the Slater determinants and these expressions are useful for quantum chemistry calculations. The variation procedure for solving Shrödinger equation is extended to optimize the coefficients in the linear sum of the symplectic bases, the parameters in the geminals, and the orbitals. For illustration, the LiH molecule, which is taken as an example, is calculated by means of the AGP, the SPG, and the AGP-SPG bases. In this paper, we also deal with the property of the symplectic bases in the dual space.

2. On geminals

Let us consider a system of N electrons associated with $2M$ spin-orbitals to which $2M$ creators a_i^+ with $i = 1, 2, \ldots, 2M$ and $2M$ annihilators a_i with $i = 1, 2, \ldots, 2M$ correspond. Furthermore, let us relabel these operators in the form

$$\begin{array}{ll} a_i^+,\ a_{\bar{\imath}}^+, & i = 1, 2, \ldots, M, \\ a_i,\ a_{\bar{\imath}}, & i = 1, 2, \ldots, M, \end{array} \tag{1}$$

where $\bar{\imath}$ is used to denote $2M + 1 - i$, i.e., $\bar{i} = 2M + 1 - i$. In this paper $a_i^+,\ a_i$ and $a_{\bar{\imath}}^+,\ a_{\bar{\imath}}$ are assigned as spin up and spin down, respectively.

Under the similarity transformation

$$R = \mathrm{e}^X \tag{2}$$

with

$$X = \sum_{i=1}^{M} \lambda_i \left(a_i^+ a_i + a_{\bar{\imath}}^+ a_{\bar{\imath}}\right) \tag{3}$$

the operators $a_i^+,\ a_{\bar{\imath}}^+,\ a_i,\ a_{\bar{\imath}}$ in equation (1) turn into the parameter-dependent form by writing

$$\begin{array}{ll} a_i^+(\xi_i) = \xi_i^{1/2} a_i^+, & a_{\bar{\imath}}^+(\xi_i) = \xi_i^{1/2} a_{\bar{\imath}}^+, \\ a_i(\xi_i) = \xi_i^{-1/2} a_i, & a_{\bar{\imath}}(\xi_i) = \xi_i^{-1/2} a_{\bar{\imath}}, \end{array} \tag{4}$$

where the complex parameters $\xi_i,\ i = 1, 2, \ldots, M$, are defined as

$$\xi_i = \mathrm{e}^{2\lambda_i}. \tag{5}$$

By means of the one-particle operators in equation (4), we can introduce, from group theory, M independent geminals, Q and $g_i,\ i = 1, 2, \ldots, M - 1$, together with their associated operators, Q', Q_0 and $g', g_{0i},\ i = 1, 2, \ldots, M - 1$, by writing

$$Q = \sum_{i=1}^{M} (-1)^i a_i^+(\xi_i) a_{\bar{\imath}}^+(\xi_i) = \sum_{i=1}^{M} (-1)^i \xi_i a_i^+ a_{\bar{\imath}}^+, \tag{6}$$

$$Q' = -\sum_{i=1}^{M}(-1)^i a_i(\xi_i)a_{\bar{\imath}}(\xi_i) = -\sum_{i=1}^{M}(-1)^i \xi_i^{-1} a_i a_{\bar{\imath}}, \tag{7}$$

$$Q_0 = \frac{1}{2}\sum_{i=1}^{M}\left[a_i^+(\xi_i)a_i(\xi_i) - a_{\bar{\imath}}(\xi_i)a_{\bar{\imath}}^+(\xi_i)\right] = \frac{1}{2}\sum_{i=1}^{M}(a_i^+ a_i - a_{\bar{\imath}} a_{\bar{\imath}}^+), \tag{8}$$

$$\begin{aligned} g_i &= \left(\frac{M-i}{M-i+1}\right)^{1/2}\left[(-1)^i a_i^+(\xi_i)a_{\bar{\imath}}^+(\xi_i) - \frac{1}{M-i}\sum_{j=i+1}^{M}(-1)^j a_j^+(\xi_j)a_{\bar{\jmath}}^+(\xi_j)\right] \\ &= \left(\frac{M-i}{M-i+1}\right)^{1/2}\left[(-1)^i \xi_i a_i^+ a_{\bar{\imath}}^+ - \frac{1}{M-i}\sum_{j=i+1}^{M}(-1)^j \xi_j a_j^+ a_{\bar{\jmath}}^+\right], \end{aligned} \tag{9}$$

$$\begin{aligned} g_i' &= \left(\frac{M-i}{M-i+1}\right)^{1/2}\left[(-1)^i a_i(\xi_i)a_{\bar{\imath}}(\xi_i) - \frac{1}{M-i}\sum_{j=i+1}^{M}(-1)^j a_j(\xi_j)a_{\bar{\jmath}}(\xi_j)\right] \\ &= \left(\frac{M-i}{M-i+1}\right)^{1/2}\left[(-1)^i \xi_i^{-1} a_i a_{\bar{\imath}} - \frac{1}{M-i}\sum_{j=i+1}^{M}(-1)^j \xi_j^{-1} a_j a_{\bar{\jmath}}\right], \end{aligned} \tag{10}$$

$$g_{0i} = \left(\frac{M-i}{2(M-i+1)}\right)^{1/2}\left[(a_{\bar{\imath}}a_{\bar{\imath}}^+ - a_i^+ a_i) - \frac{1}{M-i}\sum_{j=i+1}^{M}(a_{\bar{\jmath}}a_{\bar{\jmath}}^+ - a_j^+ a_j)\right], \tag{11}$$

where $\xi_i,\ i = 1, 2, \ldots, M$, are referred to as geminal parameters, and the quantity $\sum_{i=1}^{M}\xi_i\xi_i^*$, which is an arbitray real number, is assigned in this paper as unit without loss generality, i.e., $\sum_{i=1}^{M}\xi_i\xi_i^* = 1$. Furthermore, it is not difficult to find that the operators Q, Q', Q_0 and g_i, g_i', g_{0i} satisfy the commutation relations by writing

$$[Q, Q'] = 2Q_0, \qquad [Q_0, Q] = Q, \qquad [Q_0, Q'] = -Q', \tag{12}$$

$$[Q, g_i] = 0, \qquad [Q_0, g_i] = g_i, \qquad [Q', g_i] = \sqrt{2}g_{i0}, \tag{13}$$

$$[Q, g_{i0}] = \sqrt{2}g_i, \qquad [Q_0, g_{i0}] = 0, \qquad [Q', g_{i0}] = \sqrt{2}g_i', \tag{14}$$

$$[Q, g_i'] = \sqrt{2}g_{i0}, \qquad [Q_0, g_1'] = -g_i', \qquad [Q', g_i'] = 0. \tag{15}$$

The commutation relations in equation (12) show that, Q, Q', Q_0 act as generators to produce $SU(2)$ group, and the commutation relations in equations (13)–(15) show that $g_i,\ g_{i0}, g_i'$ satisfy the irreducible tensor commutation relations of the $SU(2)$ group with respect to $j = 1,\ m = 1, 0, -1$, i.e.,

$$\left[J_\pm, T_m^j\right] = \sqrt{j(j+1) - m(m\pm 1)}\,T_{m\pm 1}^j, \qquad \left[J_z, T_m^j\right] = mT_m^j.$$

3. The symplectic bases set

In this section, let us give a brief disscussion on the construction of $\binom{2M}{N}$ complete antisymmetrized bases set with N electrons which are built up by means of the geminals $Q, g_i,\ i = 1, 2, \dots, M-1$, and the operators $a_i^+(\xi_i), a_{\bar{\imath}}^+(\xi_i),\ i = 1, 2, \dots, M$. We shall see that the symmetry of symplectic group $Sp(2M)$ will be involved in the construction.

Taking into consideration of the one-particle operators $a_i^+(\xi_i), a_{\bar{\imath}}^+(\xi_i)$, the $M(2M+1)$ generators of symplectic group $Sp(2M)$ can be expressed as

$$E_{ij} = a_i^+(\xi_i)a_j(\xi_j) - (-1)^{i+j}a_{\bar{\jmath}}^+(\xi_j)a_{\bar{\imath}}(\xi_i), \quad i, j = 1, 2, \dots, M, \tag{16}$$

$$E_{i\bar{\jmath}} = a_i^+(\xi_i)a_{\bar{\jmath}}(\xi_j) - (-1)^{i+\bar{\jmath}}a_j^+(\xi_j)a_{\bar{\imath}}(\xi_i), \quad i \geqslant j,\ i, j = 1, 2, \dots, M, \tag{17}$$

$$E_{\bar{\imath}j} = a_{\bar{\imath}}^+(\xi_i)a_j(\xi_j) - (-1)^{\bar{\imath}+j}a_{\bar{\jmath}}^+(\xi_j)a_i(\xi_i), \quad i \geqslant j,\ i, j = 1, 2, \dots, M. \tag{18}$$

Notice that when we take $i = j$ in E_{ij} in equation (16), we have

$$E_{ii} = a_i^+ a_i - a_{\bar{\imath}}^+ a_{\bar{\imath}}, \quad i = 1, 2, \dots, M. \tag{19}$$

These M operators are referred to as the generators of the Cartan subalgebra of $Sp(2M)$. Furthermore, the Casimir operator C of $Sp(2M)$ is expressible in terms of the operators in equations (16)–(18),

$$C = \frac{1}{4}\sum_{i,j=1}^{M}\left(E_{ij}E_{ji} + \frac{1}{2}E_{i\bar{\jmath}}E_{\bar{\jmath}i} + \frac{1}{2}E_{\bar{\imath}j}E_{j\bar{\imath}}\right). \tag{20}$$

It is known, from group theory, that for a system with N-electron, the representation $[1^N]$ of unitray group $U(2M)$ can be decomposed into the representations $\{\langle 1^V\rangle\}$ of $Sp(2M)$ in the form

$$[1^N] = \sum_V \langle 1^V\rangle, \tag{21}$$

with

$$\dim\,[1^N] = \binom{2M}{N} = \sum_V \dim\,\langle 1^V\rangle \tag{22}$$

and

$$\dim\,\langle 1^V\rangle = \binom{2M}{V} - \binom{2M}{V-2}, \tag{23}$$

where $\dim\,[1^N]$ and $\dim\,\langle 1^V\rangle$ are used to denote the dimensions of the representations $[1^N]$ and $\langle 1^V\rangle$, respectively. In the summations in equations (21) and (22), the symplectic number V of $\langle 1^V\rangle$ takes the values for $N \leqslant M$,

$$V = \begin{cases} 0, 2, 4, \dots, N, & \text{for even } N, \\ 1, 3, 5, \dots, N, & \text{for odd } N, \end{cases} \tag{24}$$

for $M \leqslant N \leqslant 2M$,

$$V = \begin{cases} 0, 2, 4, \dots, 2M - N, & \text{for even } N, \\ 1, 3, 5, \dots, 2M - N, & \text{for odd } N. \end{cases} \tag{25}$$

The decomposition rule from $U(2M)$ to $Sp(2M)$ in equation (21), shows that the $\binom{2M}{N}$ complete antisymmetrized bases set of the representation $[1^N]$ can be constructed as the irreducible bases $\{|N\langle 1^V\rangle(\alpha_1, \alpha_2, \dots, \alpha_M)\rangle\}$ of the representation of $\langle 1^V\rangle$ with the weight $(\alpha_1, \alpha_2, \dots, \alpha_M)$. And these irreducible bases are the simultaneous eigenstates of the Casimir operator C in equation (20) and the operators $\{E_{ii}\}$ of Cartan subalgebra in equation (19), i.e.,

$$C\big|N\big\langle 1^V\big\rangle(\alpha_1, \alpha_2, \dots, \alpha_M)\big\rangle = \left[\frac{M}{2}\left(\frac{M}{2} + 1\right) - \frac{M - V}{2}\left(\frac{M - V}{2} + 1\right)\right] \times \big|N\big\langle 1^V\big\rangle(\alpha_1, \alpha_2, \dots, \alpha_M)\big\rangle, \tag{26}$$

$$E_{ii}\big|N\big\langle 1^V\big\rangle(\alpha_1, \alpha_2, \dots, \alpha_M)\big\rangle = \alpha_i\big|N\big\langle 1^V\big\rangle(\alpha_1, \alpha_2, \dots, \alpha_M)\big\rangle. \tag{27}$$

Notice that the ith component α_i of the weight $(\alpha_1, \alpha_2, \dots, \alpha_M)$ is the eigenvalue of the operator E_{ii}, and it takes the values $1, 0, -1$. Furthermore, the operators $a_i^+(\xi_i)$ and $a_{\bar{i}}^+(\xi_i)$ in equation (4) satisfy the commutation relations

$$\big[E_{ii}, a_j^+(\xi_j)\big] = \delta_{ij} a_j^+(\xi_j), \tag{28}$$

$$\big[E_{ii}, a_{\bar{j}}^+(\xi_j)\big] = -\delta_{ij} a_{\bar{j}}^+(\xi_j). \tag{29}$$

These relations indicate that $a_i^+(\xi_i)$ is characterized by the ith component $\alpha_i = 1$ of the weight $(0 \dots 0 \underset{i}{1} 0 \dots 0)$, $a_{\bar{i}}^+(\xi_i)$ by the ith component $\alpha_i = -1$ of the weight $(0 \dots 0 - \underset{i}{1} 0 \dots 0)$. Thus $a_i^+(\xi_i)$ and $a_{\bar{i}}^+(\xi_i)$ can be rewritten as

$$a_{i(\alpha_i)}^+(\xi_i) = \begin{cases} a_i^+(\xi_i), & \text{for } \alpha_i = 1, \\ a_{\bar{i}}^+(\xi_i), & \text{for } \alpha_i = -1. \end{cases} \tag{30}$$

Notice that $\alpha_i = 1$ and $\alpha_i = -1$ are associated with spin up and spin down, respectively.

Since

$$\big[E_{ii}, a_j^+(\xi_j) a_{\bar{j}}^+(\xi_j)\big] = 0, \tag{31}$$

the geminals Q and g_i, $i = 1, 2, \dots, M - 1$, satisfy the commutation relations

$$[E_{ii}, Q] = 0, \tag{32}$$

$$[E_{ii}, g_j] = 0. \tag{33}$$

These relations show that the geminals Q and g_i $(i = 1, 2, \dots, M-1)$ are characterized by the weight $(0 \dots 0)$.

Since some weights of the representation $\langle 1^V\rangle$ are degenerate, the group-theoretical symbol $\langle 1^V\rangle(\alpha_1,\alpha_2,\ldots,\alpha_M)$ can not provide a complete classification of the bases $\{|N\langle 1^V\rangle(\alpha_1,\alpha_2,\ldots,\alpha_M)\rangle\}$ in equations (26) and (27) with $\dim\langle 1^V\rangle$ given by equation (23). In order to give a complete classification of the bases, the irreducible representations $\langle 1^{V_1}\rangle,\langle 1^{V_2}\rangle,\ldots,\langle 1^{V_M}\rangle$ of a symplectic group chain

$$\begin{array}{llll} Sp(2M) \supset & Sp(2M-2) \supset & \cdots \supset & Sp(2) \\ \langle 1^{V_1}\rangle & \langle 1^{V_2}\rangle & \cdots & \langle 1^{V_M}\rangle \end{array} \tag{34}$$

are introduced instead of $\langle 1^V\rangle$ to extend $|N\langle 1^V\rangle(\alpha_1,\alpha_2,\ldots,\alpha_M)\rangle$ to the form $|N\langle 1^{V_1}\rangle\langle 1^{V_2}\rangle\cdots\langle 1^{V_M}\rangle(\alpha_1,\alpha_2,\ldots,\alpha_M)\rangle$. For the group chain (34), the weight $(\alpha_1,\alpha_2,\ldots,\alpha_M)$ of representation $\langle 1^{V_1}\rangle$ can be interpreted in an alternative meaning, i.e., the first component α_1 which keeps its original meaning is referred to as the first component of the weight $(\alpha_1,\alpha_2,\ldots,\alpha_M)$ of the representation $\langle 1^{V_1}\rangle$ for group $Sp(2M)$, the second component α_2 as the first component of the weight $(\alpha_2,\alpha_3,\ldots,\alpha_M)$ of the representation $\langle 1^{V_2}\rangle$ for group $Sp(2M-2),\ldots,$ the ith component α_i as the first component of the weight $(\alpha_i,\alpha_{i+1},\ldots,\alpha_M)$ of the representation $\langle 1^{V_i}\rangle$ for group $Sp(2M-2i+2)$, etc. Thus the basis set $|N\langle 1^{V_1}\rangle\langle 1^{V_2}\rangle\cdots\langle 1^{V_M}\rangle(\alpha_1,\alpha_2,\ldots,\alpha_M)\rangle$ can be rewritten as

$$\big|N\langle 1^{V_1}\rangle(\alpha_1)\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\big\rangle, \tag{35}$$

where the symbol (α) attached to $\langle 1^V\rangle$ as $\langle 1^V\rangle(\alpha)$ denotes the first component of the corresponding weight $(\alpha\ldots)$ and α takes the values $1,0,-1$. Furthermore, the symbol $\langle 1^V\rangle(\alpha)$ means that the bases, which belong to the representation $\langle 1^V\rangle$, can be classified by means of $\langle 1^V\rangle(1),\langle 1^V\rangle(0)$ and $\langle 1^V\rangle(-1)$ such that

$$\langle 1^V\rangle = \begin{cases} \langle 1^V\rangle(1), \\ \langle 1^V\rangle(0), \\ \langle 1^V\rangle(-1) \end{cases} \tag{36}$$

with

$$\dim\langle 1^V\rangle = \dim\langle 1^V\rangle(1) + \dim\langle 1^V\rangle(0) + \dim\langle 1^V\rangle(-1), \tag{37}$$

where the dimensions $\dim\langle 1^V\rangle(1)$, $\dim\langle 1^V\rangle(0)$ and $\dim\langle 1^V\rangle(-1)$ with respect to $\langle 1^V\rangle(1)$, $\langle 1^V\rangle(0)$ and $\langle 1^V\rangle(-1)$ are given by writing

$$\dim\langle 1^V\rangle(\pm 1) = \frac{V(M-V+1)}{M(2M-V+1)}\binom{2M}{V}, \tag{38}$$

$$\dim\langle 1^V\rangle(0) = \frac{2(M-V+1)[M(2M+1)-2(M+1)V+V^2]}{(2M-V+2)(2M-V+1)}\binom{2M}{V}. \tag{39}$$

A complete group-theoretical classification of the basis set in equation (35) can be illustrated by the modified branching rules

$$Sp(2M) \longrightarrow Sp(2M-2),$$

$$\langle 1^{V_1}\rangle(\pm 1) \longrightarrow \big(1-\delta_{V_1,0}\big)\langle 1^{V_1-1}\rangle, \tag{40}$$

$$\langle 1^{V_1}\rangle(0) \longrightarrow \big(1-\delta_{V_1,M}\big)\langle 1^{V_1}\rangle + \big(1-\delta_{V_1,1}-\delta_{V_1,0}\big)\langle 1^{V_1-2}\rangle. \tag{41}$$

These branching rules, which play in this paper a crucial role, hold true for $Sp(2M-2i+2) \to Sp(2M-2i)$ with $i = 1, 2, \ldots, M-1$.

By the similar method in the earlier publication [20], the basis set in equation (35) can be constructed in terms of the geminals Q in equation (6) and g_i with $i = 1, 2, \ldots, M-1$ in equation (9), and the $2M$ operators $a_i^+(\xi_i)$ and $a_{\bar{i}}^+(\xi_i)$ in equation (4). The basis set

$$\big\{\big|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\big\rangle\big\}$$

takes the form

$$\begin{aligned}&\big|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\big\rangle\\&\quad = C(M,N,V_1)Q^{(N-V_1)/2}\prod_{i=1}^{M} G(i,V_i,\alpha_i)a^+(i,V_i,\alpha_i)|0\rangle,\end{aligned} \tag{42}$$

where $C(M,N,V_1)$ is the normalization constant

$$C(M,N,V_1) = \left[\frac{\big(M-V_1-\frac{N-V_1}{2}\big)!}{(M-V_1)!\big(\frac{N-V_1}{2}\big)!}\right]^{1/2} \tag{43}$$

and where $G(i,V_i,\alpha_i)$ and $a^+(i,V_i,\alpha_i)$ are defined as

$$a^+(i,V_i,\alpha_i) = \begin{cases} 1, & \text{for } V_i \neq V_{i+1}+1,\ \alpha_i \neq \pm 1,\\ a^+_{i(\alpha_i)}(\xi_i), & \text{for } V_i = V_{i+1}+1,\ \alpha_i = \pm 1,\end{cases} \tag{44}$$

$$G(i,V_i,\alpha_i) = \begin{cases} 1, & \text{for } V_i \neq V_{i+1}+2,\ \alpha_i \neq 0,\\ G(i,V_{i+1}), & \text{for } V_i = V_{i+1}+2,\ \alpha_i = 0.\end{cases} \tag{45}$$

In equation (45), $G(i,V_{i+1})$ is expressible as a linear sum of the geminals, Q and g_k $(k = 1, 2, \ldots, i)$, by writing

$$\begin{aligned}G(i,V_{i+1}) = {}& A_i\left\{\frac{1}{M}Q - \sum_{k=1}^{i-1}\big[(M-k+1)(M-k)\big]^{-1/2}g_k + \left(\frac{M-i}{M-i+1}\right)^{1/2}g_i\right\}\\&- B_i(M-i)\left\{\frac{1}{M}Q - \sum_{k=1}^{i}\big[(M-k-1)(M-k)\big]^{-1/2}g_k\right\},\\&i = 1, 2, \ldots, M-1,\end{aligned} \tag{46}$$

with

$$A_i = \left[\frac{M-i-V_{i+1}}{M-i-V_{i+1}+1}\right]^{1/2}, \tag{47}$$

$$B_i = \left[(M - i - V_{i+1})(M - i - V_{i+1} + 1)\right]^{-1/2}. \tag{48}$$

The expression in equation (46) can be rewritten in the simple form

$$G(i, V_{i+1}) = A_i b_i^+(\xi_i) - B_i \sum_{j=i+1}^{M} b_j^+(\xi_j) \tag{49}$$

with

$$b_k^+(\xi_k) = (-1)^k \xi_k b_k^+, \qquad b_k^+ = a_k^+ a_{\bar{k}}^+, \quad k = 1, 2, \ldots, M. \tag{50}$$

In equation (42), Q in equation (6) is referred to as the first kind geminal, and $G(i, V_{i+1})$ in equation (49) with $i = 1, 2, \ldots, M-1$ are referred to as the second kind geminal. Notice that for a given basis $|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)$ the group symbol $\langle 1^{V_i}\rangle(\alpha_i)$ $i = 1, 2, \ldots, M$ arise from the branching rules in equations (40)–(41). Furthermore, from the expression of the symplectic bases in equation (42), we can obtain directly the following form

$$\begin{aligned} &\big|\big\langle 1^{V_1}\big\rangle(\alpha_i)\,\big\langle 1^{V_2}\big\rangle(\alpha_2)\cdots\big\langle 1^{V_M}\big\rangle(\alpha_M)\big\rangle \\ &\quad = C(M, N, V_1) Q^{(N-V_1)/2} \prod_{L=1}^{(V_1-X)/2} G(j_L, V_{j_L+1}) \prod_{k=1}^{X} a^+_{i_k(\alpha_{i_k})}(\xi_{i_k})|0\rangle, \end{aligned} \tag{51}$$

where X is defined as

$$X = \sum_{i=1}^{M} |\alpha_i| \tag{52}$$

and it takes the values as

$$X = \begin{cases} 0, 2, 4, \ldots, V_1, & \text{for even } N, \\ 1, 3, 5, \ldots, V_1, & \text{for odd } N. \end{cases} \tag{53}$$

In equation (51), the fixed indices $(j_1, j_2, \ldots, j_{(V_1-X)/2})$ and $(i_1, i_2 \ldots, i_X)$ are subject to the relations

$$j_1 < j_2 < \cdots < j_{(V_1-X)/2}, \quad j_1, j_2, \ldots, j_{(V_1-X)/2} = 1, 2, \ldots, M-1, \tag{54}$$

$$i_1 < i_2 < \cdots < i_X, \quad i_1, i_2, \ldots, i_X = 1, 2, \ldots, M, \tag{55}$$

$$(j_1, j_2, \ldots, j_{(V_1-X)/2}) \cap (i_1, i_2, \ldots, i_x) = \emptyset \quad \text{(empty set)}. \tag{56}$$

Since the first and the second kind geminals, Q and $\{G(i, V_{i+1})\}$ are characterized by $\alpha_i = 0$ as shown in equations (32) and (33) and the one-particle operators $\{a^+_{i_k(\alpha_{i_k})}(\xi_{i_k})\}$ are characterized by $\alpha_{i_k} = \pm 1$ as shown in equation (30), the quantity X in equation (52) is just the number of the one-particle operators. The expression in equation (51) shows that for a given basis $|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle$, it possesses $(N - V_1)/2$ the first kind geminal Q, $(V_1 - X)/2$ the second kind geminal

$\{G(i, V_{i+1})\}$ and X the one-particle operators $\{a^+_{i_k(\alpha_{i_k})}(\xi_{i_k})\}$. For brevity, we only state without proof that, the total number of the second kind geminal $\{G(i, V_{i+1})\}$ which appears in $\binom{2M}{N}$ bases set, is $[(N-1)(2M-N-1)+1]/2$ for even N or $(N-1)(2M-N-1)/2$ for odd N. Notice that in the first and the second kind geminals, there are only M independent ones.

For illustration of the basis set in equation (42), we take $Sp(8)$ with $M = 4$ and $N = 4$ in which there are $\binom{8}{4} = 70$ bases as an example. In this example, we shall further discuss the types of the symplectic bases such as AGP, SPG, AGP-SPG, GAGP, GSPG, SD and G(AGP-SPG).

3.1. *AGP (Antisymmetrized Geminal Power)*

There is only one AGP basis with $V_1 = 0$ and $X = 0$ in the form

$$\big|4\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\big\rangle = \frac{1}{\sqrt{4!}}Q^2|0\rangle.$$

In the general case of $\binom{2M}{N}$ with even N, there is only one AGP

$$\big|N\langle 0\rangle(0)\,\langle 0\rangle(0)\cdots\langle 0\rangle(0)\big\rangle = \left(\frac{\left(M-\frac{N}{2}\right)!}{M!\left(\frac{N}{2}\right)!}\right)^{1/2} Q^{N/2}|0\rangle, \tag{57}$$

in which only the first kind geminal Q is involved, and for group $Sp(2M)$, the AGP is characterized by $V_1 = 0$ and $X = 0$. When N is odd, there is no AGP appearing in the bases $\binom{2M}{N}$.

3.2. *SPG (Sequential Product of Geminals)*

There are two SPG bases with $V_1 = N = 4$ and $X = 0$ such that

$$\big|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\big\rangle = G(1,2)G(2,0)|0\rangle,$$

$$\big|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(0)\,\langle 1^2\rangle(0)\,\langle 0\rangle(0)\big\rangle = G(1,2)G(3,0)|0\rangle.$$

In the general case of $\binom{2M}{N}$ with even N and $N \leqslant M$, there are

$$\binom{M}{N/2} - \binom{M}{N/2-1} \tag{58}$$

SPG bases in which only the second kind geminal is involved, and for group $Sp(2M)$, the SPG bases are characterized by $V_1 = N$ and $X = 0$. When N in equation (58) is replaced by $2M - N$, equation (58) still holds true for the case of $M \leqslant N \leqslant 2M$. When N is odd, there is no SPG appearing in the bases $\binom{2M}{N}$.

3.3. AGP-SPG

There are three AGP-SPG bases with $V_1 = 2$ and $X = 0$ such that

$$\left|4\langle 1^2\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\right\rangle = \frac{1}{\sqrt{2}}QG(1,0)|0\rangle,$$

$$\left|4\langle 1^2\rangle(0)\,\langle 1^2\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\right\rangle = \frac{1}{\sqrt{2}}QG(2,0)|0\rangle,$$

$$\left|4\langle 1^2\rangle(0)\,\langle 1^2\rangle(0)\,\langle 1^2\rangle(0)\,\langle 0\rangle(0)\right\rangle = \frac{1}{\sqrt{2}}QG(3,0)|0\rangle.$$

In the general case of $\binom{2M}{N}$ with even N and $N \leqslant M$, there are

$$\sum_{V_1=2,4,\ldots}^{N-2} \binom{M}{V_1/2} - \binom{M}{V_1/2-1} \tag{59}$$

AGP-SPG bases in which both the first and the second kind geminals are involved, and for group $Sp(2M)$, the AGP-SPG bases are characterized by $V_1 = 2, 4, \ldots, N-2$ and by $X = 0$. When $N-2$ in the summation in equation (59) is replaced by $2M-N-2$, equation (59) still holds true for the case of $M \leqslant N \leqslant 2M$. When N is odd, there is no AGP-SPG appearing in the bases $\binom{2M}{N}$.

3.4. GAGP (Generalized Antisymmetrized Geminal Power)

There are 24 GAGP bases with $V_1 = 2$ and $X = 2$ such that

$$\left|4\langle 1^2\rangle(\pm1)\,\langle 1\rangle(\pm1)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\right\rangle = \frac{1}{\sqrt{2}}Qa^+_{1(\pm1)}(\xi_1)a^+_{2(\pm1)}(\xi_2)|0\rangle,$$

$$\left|4\langle 1^2\rangle(\pm1)\,\langle 1\rangle(0)\,\langle 1\rangle(\pm1)\,\langle 0\rangle(0)\right\rangle = \frac{1}{\sqrt{2}}Qa^+_{1(\pm1)}(\xi_1)a^+_{3(\pm1)}(\xi_3)|0\rangle,$$

$$\left|4\langle 1^2\rangle(\pm1)\,\langle 1\rangle(0)\,\langle 1\rangle(0)\,\langle 1\rangle(\pm1)\right\rangle = \frac{1}{\sqrt{2}}Qa^+_{1(\pm1)}(\xi_1)a^+_{4(\pm1)}(\xi_4)|0\rangle,$$

$$\left|4\langle 1^2\rangle(0)\,\langle 1^2\rangle(\pm1)\,\langle 1\rangle(\pm1)\,\langle 0\rangle(0)\right\rangle = \frac{1}{\sqrt{2}}Qa^+_{2(\pm1)}(\xi_2)a^+_{3(\pm1)}(\xi_3)|0\rangle,$$

$$\left|4\langle 1^2\rangle(0)\,\langle 1^2\rangle(\pm1)\,\langle 1\rangle(0)\,\langle 1\rangle(\pm1)\right\rangle = \frac{1}{\sqrt{2}}Qa^+_{2(\pm1)}(\xi_2)a^+_{4(\pm1)}(\xi_4)|0\rangle,$$

$$\left|4\langle 1^2\rangle(0)\,\langle 1^2\rangle(0)\,\langle 1^2\rangle(\pm1)\,\langle 1\rangle(\pm1)\right\rangle = \frac{1}{\sqrt{2}}Qa^+_{3(\pm1)}(\xi_3)a^+_{4(\pm1)}(\xi_4)|0\rangle.$$

In the general case of $\binom{2M}{N}$ with even or odd N and $N \leqslant M$, there are

$$\sum_{\substack{X=2,4,\ldots \\ \text{or } 1,3,\ldots}}^{N-2} 2^X \binom{M}{X} \tag{60}$$

GAGP bases in which the first kind geminal Q and the one-particle operators $\{a^+_{i(\alpha_i)}(\xi_i)\}$ are involved, and for group $Sp(2M)$, the GAGP bases are characterized by $V_1 = X = 2, 4, \ldots, N-2$ for even N or $1, 3, \ldots, N-2$ for odd N. When $N-2$ in the summation in equation (60) is replaced by $2M-N-2$, equation (60) still holds true for the case of $M \leqslant N \leqslant 2M$.

3.5. *GSPG (Generalized Sequential Product of Geminals)*

There are 24 GSPG bases with $V_1 = 4$ and $X = 2$ such that

$$\left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(\pm 1)\,\langle 1\rangle(\pm 1)\,\langle 0\rangle(0)\right\rangle = G(1,2)a^+_{2(\pm 1)}(\xi_2)a^+_{3(\pm 1)}(\xi_3)|0\rangle,$$

$$\left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(\pm 1)\,\langle 1\rangle(0)\,\langle 1\rangle(\pm 1)\right\rangle = G(1,2)a^+_{2(\pm 1)}(\xi_2)a^+_{4(\pm 1)}(\xi_4)|0\rangle,$$

$$\left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(0)\,\langle 1^2\rangle(\pm 1)\,\langle 1\rangle(\pm 1)\right\rangle = G(1,2)a^+_{3(\pm 1)}(\xi_3)a^+_{4(\pm 1)}(\xi_4)|0\rangle,$$

$$\left|4\langle 1^4\rangle(\pm 1)\,\langle 1^3\rangle(\pm 1)\,\langle 1^2\rangle(0)\,\langle 0\rangle(0)\right\rangle = a^+_{1(\pm 1)}(\xi_1)a^+_{2(\pm 1)}(\xi_2)G(3,0)|0\rangle,$$

$$\left|4\langle 1^4\rangle(\pm 1)\,\langle 1^3\rangle(0)\,\langle 1\rangle(\pm 1)\,\langle 0\rangle(0)\right\rangle = a^+_{1(\pm 1)}(\xi_1)G(2,1)a^+_{3(\pm 1)}(\xi_3)|0\rangle,$$

$$\left|4\langle 1^4\rangle(\pm 1)\,\langle 1^3\rangle(0)\,\langle 1\rangle(0)\,\langle 1\rangle(\pm 1)\right\rangle = a^+_{1(\pm 1)}(\xi_1)G(2,1)a^+_{4(\pm 1)}(\xi_4)|0\rangle.$$

In the general case of $\binom{2M}{N}$ with even or odd N and $N \leqslant M$, there are

$$\sum_{\substack{X=2,4,\ldots \\ \text{or } 1,3,\ldots}}^{N-2} 2^X \binom{M}{X}\left(\binom{M-X}{(N-X)/2} - \binom{M-X}{(N-X)/2-1}\right) \tag{61}$$

GSPG bases in which the second kind geminals $\{G(i, V_{i+1})\}$ and the one-particle operators $\{a^+_{i(\alpha_i)}(\xi_i)\}$ are involved, and for group $Sp(2M)$, the GSPG bases are characterized by $V_1 = N$, and $X = 2, 4, \ldots, N-2$ for even N or $X = 1, 3, \ldots, N-2$ for odd N. When $N-2$ in the summation in equation (61) is replaced by $2M-N-2$, equation (61) still holds true for the case of $M \leqslant N \leqslant 2M$.

3.6. *SD (Slater Determinant)*

There are 16 SD bases with $V_1 = X = 4$ by writing

$$\left|4\langle 1^4\rangle(\pm 1)\,\langle 1^3\rangle(\pm 1)\,\langle 1^2\rangle(\pm 1)\,\langle 1\rangle(\pm 1)\right\rangle = a^+_{1(\pm 1)}(\xi_1)a^+_{2(\pm 1)}(\xi_2)a^+_{3(\pm 1)}(\xi_3)a^+_{4(\pm 1)}(\xi_4)|0\rangle.$$

In the general case of $\binom{2M}{N}$ with even or odd N and $N \leqslant M$, there are

$$2^N \binom{M}{N} \tag{62}$$

SD bases in which only the one-particle operators $\{a^+_{i(\alpha_i)}(\xi_i)\}$ are involved, and for group $Sp(2M)$, the SD bases are characterized by $V_1 = X = N$. When N in equation (62) is replaced by $2M - N$, equation (62) still holds true for the case of $M \leqslant N \leqslant 2M$.

3.7. G(AGP-SPG) (Generalized AGP-SPG)

For group $Sp(8)$ with $M = 4$ and $N = 4$, there is no G(AGP-SPG) appearing in the 70 bases. For this, we take $Sp(12)$ with $N = 6$ as an example. In this example, there are 180 G(AGP-SPG) bases with $V_1 = 4$ and $X = 2$. For brevity, we only give twelve of them as follows

$$\begin{aligned}&\big|6\langle 1^4\rangle(\pm 1)\,\langle 1^3\rangle(\pm 1)\,\langle 1^2\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\big\rangle\\ &\quad = \frac{1}{\sqrt{2}} Q a^+_{1(\pm 1)}(\xi_1) a^+_{2(\pm 1)}(\xi_2) G(3,0)|0\rangle,\end{aligned}$$

$$\begin{aligned}&\big|6\langle 1^4\rangle(0)\,\langle 1^2\rangle(\pm 1)\,\langle 1\rangle(0)\,\langle 1\rangle(\pm 1)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\big\rangle\\ &\quad = \frac{1}{\sqrt{2}} Q G(1,0) a^+_{2(\pm 1)}(\xi_2) a^+_{4(\pm 1)}(\xi_4)|0\rangle,\end{aligned}$$

$$\begin{aligned}&\big|6\langle 1^4\rangle(0)\,\langle 1^4\rangle(0)\,\langle 1^2\rangle(\pm 1)\,\langle 1\rangle(0)\,\langle 1\rangle(0)\,\langle 1\rangle(\pm 1)\big\rangle\\ &\quad = \frac{1}{\sqrt{2}} Q G(2,2) a^+_{3(\pm 1)}(\xi_3) a^+_{6(\pm 1)}(\xi_6)|0\rangle.\end{aligned}$$

In the general case of $\binom{2M}{N}$ with even or odd N and $N \leqslant M$, there are

$$\sum_{\substack{V_1=4,6,\ldots\\ \text{or } 3,5,\ldots}}^{N-2} \; \sum_{\substack{X=2,4,\ldots\\ \text{or } 1,3,\ldots}}^{V_1-2} 2^X \binom{M}{X} \left(\binom{M-X}{(V_1-X)/2} - \binom{M-X}{(V_1-X)/2-1} \right) \tag{63}$$

G(AGP-SPG) bases in which the first and the second kind geminals, and the one-particle operators are involved, and for group $Sp(2M)$, these bases are characterized by $V_1 = 4, 6, \ldots, N-2$ and $X = 2, 4, \ldots, V_1 - 2$ for even N or $V_1 = 3, 5, \ldots, N-2$ and $X = 1, 3, \ldots, V_1 - 2$ for odd N. When $N-2$ in the summation in equation (63) is replaced by $2M - N - 2$, equation (63) still holds true for the case of $M \leqslant N \leqslant 2M$.

The sum of all types of the symplectic bases is equal to $\binom{2M}{N}$, i.e.,

$$\binom{2M}{N} = \sum_{V_1}^{N(2M-N)} \sum_{X}^{V_1} 2^X \binom{M}{X} \left(\binom{M-X}{(V_1-X)/2} - \binom{M-X}{(V_1-X)/2-1} \right)$$

$$= \sum_{V_1}^{N(2M-N)} \left(\binom{2M}{V_1} - \binom{2M}{V_1 - 2} \right), \tag{64}$$

where V_1 and X take the values given by equation (24) (equation (25)) and equation (53), respectively.

4. The symplectic bases in dual space

In this section, we shall discuss the relation between the adjoint bases $\{(|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle)^+\}$ of the bases in equation (42) and the symplectic bases in dual space.

By the similar group theoretical method as we have done in section 3, we can construct $\binom{2M}{N}$ symplectic bases $\{\langle(\alpha_M)\langle 1^{V_M}\rangle\cdots(\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N|\}$ in the dual space, which are orthogonal to the bases $\{|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle\}$ given by equation (42). By means of the M operators Q' in equation (7) and g'_i, $i = 1, 2, \ldots, M-1$, in equation (10), and $2M$ operators $a_i(\xi_i)$ and $a_{\bar{i}}(\xi_i)$ in equation (4), the bases in dual space can be written as

$$\begin{aligned} &\big\langle(\alpha_M)\langle 1^{V_M}\rangle\cdots(\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\big| \\ &\quad = C(M,N,V_1)\langle 0|Q'^{(N-V_1)/2}\prod_{i=1}^{M} G'(i,V_i,\alpha_i)a(i,V_i,\alpha_i), \end{aligned} \tag{65}$$

where the normalization constant $C(M,N,V_1)$ is given by equation (43), and

$$a(i,V_i,\alpha_i) = \begin{cases} 1, & \text{for } V_i \neq V_{i+1}+1,\ \alpha_i \neq \pm 1, \\ a_{i(\alpha_i)}(\xi_i), & \text{for } V_i = V_{i+1}+1,\ \alpha_i = \pm 1, \end{cases} \tag{66}$$

$$G'(i,V_i,\alpha_i) = \begin{cases} 1, & \text{for } V_i \neq V_{i+1}+2,\ \alpha_i \neq 0, \\ G'(i,V_{i+1}), & \text{for } V_i = V_{i+1}+2,\ \alpha_i = 0. \end{cases} \tag{67}$$

In equation (67), $G'(i,V_{i+1})$ is expressible as a linear sum of the operators Q' and g'_k $(k = 1, 2, \ldots, i)$ by writing

$$\begin{aligned} G'(i,V_{i+1}) = {} & A_i\left\{\frac{1}{M}Q' + \sum_{k=1}^{i-1}\big[(M-k)(M-k+1)\big]^{-1/2}g'_k - \left(\frac{M-i}{M-i+1}\right)^{1/2}g'_i\right\} \\ & - B_i(M-i)\left\{\frac{1}{M}Q' + \sum_{k=1}^{i}\big[(M-k)(M-k+1)\big]^{-1/2}g'_k\right\}, \\ & i = 1, 2, \ldots, M-1. \end{aligned} \tag{68}$$

This expression can be rewritten in the simple form

$$G'(i, V_{i+1}) = A_i b_i(\xi_i) - B_i \sum_{j=i+1}^{M} b_j(\xi_j) \tag{69}$$

with

$$b_k(\xi_k) = (-1)^k \xi_k^{-1} b_k, \quad b_k = a_{\overline{k}} a_k, \; k = 1, 2, \ldots, M, \tag{70}$$

where A_i and B_i are given by equations (47) and (48), respectively.

Furthermore, from the expression of the symplectic bases in dual space in equation (65), we can obtain directly the following form

$$\begin{aligned} &\big\langle (\alpha_M)\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\big| \\ &\quad = C(M, N, V_1)\langle 0|Q'^{(N-V_1)/2} \prod_{L=1}^{(V_1-X)/2} G'(j_L, V_{j_L+1}) \prod_{k=1}^{X} a_{i_k(\alpha_{i_k})}(\xi_{i_k}), \end{aligned} \tag{71}$$

where X is defined as in equation (52) and the values of X are given by equation (53).

Since $a_{i(\alpha_i)}(\xi_i)$ in equation (4) is not the adjoint operator of $a^+_{i(\alpha_i)}(\xi_i)$ in equation (4), Q' in equation (7) not the adjoint operator of Q in equation (6) and $G'(i, V_{i+1})$ in equation (69) not the adjoint operator of $G(i, V_{i+1})$ in equation (49), i.e.,

$$\big(a^+_{i(\alpha_i)}(\xi_i)\big)^+ \neq a_{i(\alpha_i)}(\xi_i), \quad Q^+ \neq Q', \quad \big(G(i, V_{i+1})\big)^+ \neq G'(i, V_{i+1}). \tag{72}$$

It is obvious that $\langle(\alpha_M)\,\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle\,(\alpha_1)\langle 1^{V_1}\rangle N|$ in dual space is not the adjoint basis of $|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle$, i.e.,

$$\begin{aligned} &\big(\big|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle\big)^+ \\ &\quad \neq \langle(\alpha_M)\,\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N|. \end{aligned} \tag{73}$$

Only under the extreme case where $\xi_i = 1, \; i = 1, 2, \ldots, M$, we have

$$\begin{aligned} &\big(\big|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle\big)^+ \\ &\quad = \langle(\alpha_M)\,\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N|. \end{aligned} \tag{74}$$

Now let us the symbol $\langle[(\alpha_M)\,\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N]|$ to denote the adjoint basis $(|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle)^+$, i.e.,

$$\begin{aligned} &\big\langle\big[(\alpha_M)\,\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\big]\big| \\ &\quad = \big(\big|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle\big)^+. \end{aligned} \tag{75}$$

From equations (51) and (75), we can obtain immediately the adjoint basis in the form

$$\big\langle\big[(\alpha_M)\,\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\big]\big|$$

$$= C(M,N,V_1)\langle 0|(Q^+)^{(N-V_1)/2}\prod_{L=1}^{(V_1-X)/2}\big(G(j_L,V_{j_{L+1}})\big)^+\prod_{k=1}^{X}\big(a^+_{i_k(\alpha_{i_k})}(\xi_{i_k})\big)^+ \quad (76)$$

with

$$Q^+ = \sum_{i=1}^{M}(-1)^i\xi_i^* b_i, \quad \big(a^+_{i_k(\alpha_{i_k})}(\xi_{i_k})\big)^+ = (\xi_{i_k}^*)^{1/2}a_{i_k(\alpha_{i_k})}, \quad (77)$$

$$\big(G(j_L,V_{j_{L+1}})\big)^+ = A_{j_L}(-1)^{j_L}\xi_{j_L}^* b_{j_L} - B_{j_L}\sum_{k=j_L+1}^{M}(-1)^k\xi_k^* b_k, \quad (78)$$

where Q^+ and $(G(j_L,V_{j_{L+1}}))^+$ are the adjoint of the geminals Q and $G(j_L,V_{j_{L+1}})$, respectively, and $(a^+_{i_k(\alpha_{i_k})}(\xi_{i_k}))^+$ is the adjoint of the operator $a^+_{i_k(\alpha_{i_k})}(\xi_{i_k})$. It should be noted that in the adjoint basis in equation (76), there are $(N-V_1)/2$ the first kind adjoint geminal, $(V_1-X)/2$ the second kind adjoint geminal, and X the adjoint one-particle operators. It is obvious that the equations (57)–(63) for the classification of AGP, SPG, AGP-SPG, GAGP, GSPG, SD and G(AGP-SPG) hold true for the adjoint bases in equation (76). Furthermore, the adjoint basis $\langle[(\alpha_M)\langle 1^{V_M}\rangle\cdots(\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N]|$ can be expanded as a linear sum of the symplectic bases given by equation (65) in the dual space in the form

$$\begin{aligned}&\big\langle\big[(\alpha_M)\langle 1^{V_M}\rangle\cdots(\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\big]\big|\\&\quad=\sum_{\{V_i',\alpha_i'\}}\Big(\big\langle\big[(\alpha_M)\langle 1^{V_M}\rangle\cdots(\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\big]\big|\\&\qquad\qquad N\langle 1^{V_1'}\rangle(\alpha_1')\langle 1^{V_2'}\rangle(\alpha_2')\cdots\langle 1^{V_M'}\rangle(\alpha_M')\big\rangle\Big)\\&\qquad\qquad\times\big\langle(\alpha_M')\langle 1^{V_M'}\rangle\cdots(\alpha_2')\langle 1^{V_2'}\rangle(\alpha_1')\langle 1^{V_1'}\rangle N\big|,\end{aligned} \quad (79)$$

where

$$\big\langle\big[(\alpha_M)\langle 1^{V_M}\rangle\cdots(\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\big]\big|N\langle 1^{V_1'}\rangle(\alpha_1')\langle 1^{V_2'}\rangle(\alpha_2')\cdots\langle 1^{V_M'}\rangle(\alpha_M')\big\rangle$$

is the expansion coefficient, and it can be evaluated by means of equations (51) and (76).

For illustrations, we take two bases for $Sp(8)$ with $N=4$ as examples.

$$\begin{aligned}&\big\langle\big[(0)\langle 0\rangle(0)\langle 1^2\rangle(1)\langle 1^3\rangle(1)\langle 1^4\rangle 4\big]\big|\\&\quad=\frac{1}{2}(\xi_1\xi_1^*)^{1/2}(\xi_2\xi_2^*)^{1/2}\big[(\xi_3\xi_3^*+\xi_4\xi_4^*)\langle(0)\langle 0\rangle(0)\langle 1^2\rangle(1)\langle 1^3\rangle(1)\langle 1^4\rangle 4\big|\\&\qquad+(\xi_3\xi_3^*-\xi_4\xi_4^*)\langle(0)\langle 0\rangle(0)\langle 0\rangle(1)\langle 1\rangle(1)\langle 1^2\rangle 4\big|\big],\end{aligned}$$

$$\begin{aligned}&\big\langle\big[(0)\langle 0\rangle(0)\langle 0\rangle(1)\langle 1\rangle(1)\langle 1^2\rangle 4\big]\big| \\ &\quad= \frac{1}{2}(\xi_1\xi_1^*)^{1/2}(\xi_2\xi_2^*)^{1/2}\big[(\xi_3\xi_3^* - \xi_4\xi_4^*)\langle(0)\langle 0\rangle(0)\langle 1^2\rangle(1)\langle 1^3\rangle(1)\langle 1^4\rangle 4\big| \\ &\qquad+ (\xi_3\xi_3^* + \xi_4\xi_4^*)\langle(0)\langle 0\rangle(0)\langle 0\rangle(1)\langle 1\rangle(1)\langle 1^2\rangle 4\big|\big].\end{aligned}$$

From equation (79), the matrix element of the Hamiltonian H for a system with N electrons can be expressed as

$$\begin{aligned}&\big\langle\big[(\alpha_M)\langle 1^{V_M}\rangle\cdots(\alpha_1)\langle 1^{V_1}\rangle N\big]\big|H\big|N\langle 1^{V_1'}\rangle(\alpha_1')\cdots\langle 1^{V_M'}\rangle(\alpha_M')\big\rangle \\ &\quad= \sum_{\{V_i'',\alpha_i''\}}\big\langle\big[(\alpha_M)\langle 1^{V_M}\rangle\cdots(\alpha_1)\langle 1^{V_1}\rangle N\big]\big|N\langle 1^{V_1''}\rangle(\alpha_1'')\cdots\langle 1^{V_M''}\rangle(\alpha_M'')\big\rangle \\ &\qquad\big\langle(\alpha_M'')\langle 1^{V_M''}\rangle\cdots(\alpha_1'')\langle 1^{V_1''}\rangle N\big|H\big|N\langle 1^{V_1'}\rangle(\alpha_1')\cdots\langle 1^{V_M'}\rangle(\alpha_M')\big\rangle, \qquad (80)\end{aligned}$$

where the matrix element

$$\big\langle(\alpha_M'')\langle 1^{V_M''}\rangle\cdots(\alpha_1'')\langle 1^{V_1''}\rangle N\big|H\big|N\langle 1^{V_1'}\rangle(\alpha_1')\cdots\langle 1^{V_M'}\rangle(\alpha_M')\big\rangle \qquad (81)$$

can be evaluated by means of the irreducible tensor method. In this paper, we shall not go further into this method.

Similarly, the adjoint of the basis in dual space can be expressed in terms of the symplectic bases in equation (42), i.e.,

$$\begin{aligned}&\big|\big[N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\big]\big\rangle \\ &\quad= \Big(\big\langle(\alpha_M)\,\langle 1^{V_M}\rangle\cdots(\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\big|\Big)^+ \\ &\quad= \sum_{\{V_i',\alpha_i'\}}\big|N\langle 1^{V_1'}\rangle(\alpha_1')\langle 1^{V_2'}\rangle(\alpha_2')\cdots\langle 1^{V_M'}\rangle(\alpha_M')\big\rangle \\ &\qquad\times\Big(\big\langle(\alpha_M')\langle 1^{V_M'}\rangle\cdots(\alpha_2')\langle 1^{V_2'}\rangle(\alpha_1')\langle 1^{V_1'}\rangle N\big| \\ &\qquad\big[N\langle 1^{V_1}\rangle(\alpha_1)\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\big]\big\rangle\Big). \qquad (82)\end{aligned}$$

5. The symplectic bases and determinant bases

In this section, we shall discuss the expansion of the symplectic bases as a linear sum of the Slater determinants, and this expansion expression is useful in making use of the quantum chemistry programs for practical calculations.

From the expression of the symplectic bases in equation (51), it is not difficult to find that the symplectic bases can be expressed as a linear sum of the determinants $b_{m_1}^+\cdots b_{m_n}^+ a_{i_1(\alpha_{i_1})}^+\cdots a_{i_X(\alpha_{i_X})}^+|0\rangle$ with $n = (N - X)/2$, where the operators $b^+_{m_1} \cdots b^+_{m_n}$ arise from the expansion of the first and the second kind geminals, Q and $\{G(j_L, V_{j_{L+1}})\}$, and where the one-particle operators $a^+_{i_1(\alpha_{i_1})} \cdots a^+_{i_X(\alpha_{i_X})}$ keep the same order of $a^+_{i_1(\alpha_{i_1})}(\xi_{i_1}) \cdots a^+_{i_X(\alpha_{i_X})}(\xi_{i_X})$ appearing in equation (51) with $a^+_{i_k(\alpha_{i_k})}(\xi_{i_k}) = \xi^{1/2}_{i_k} a^+_{i_k(\alpha_{i_k})}$, $k = 1, 2, \ldots, X$. From equation (51), we can obtain, by induction,

$$\begin{aligned}
&\big|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\big\rangle \\
&\quad = C(M,N,V_1)Q^{n-y}\prod_{L=1}^{y} G(j_L, V_{j_L+1})\prod_{k=1}^{X} a^+_{i_k(\alpha_{i_k})}(\xi_{i_k})|0\rangle \\
&\quad = C(M,N,V_1)\sum_{m_1,m_2,\ldots,m_n} D_{m_1m_2\ldots m_n i_1 i_2\ldots i_X} E_{m_1m_2\ldots m_n j_1 j_2\ldots j_y} \\
&\qquad\qquad \times b^+_{m_1} b^+_{m_2}\cdots b^+_{m_n} a^+_{i_1(\alpha_{i_1})} a^+_{i_2(\alpha_{i_2})}\ldots a^+_{i_X(\alpha_{i_X})}|0\rangle,
\end{aligned} \tag{83}$$

where $n = (N - X)/2$, $y = (V_1 - X)/2$, $n - y = (N - V_1)/2$, and $D_{m_1m_2\ldots m_n\, i_1 i_2\ldots i_X}$ is expressible in terms of the geminal parameters

$$D_{m_1m_2\ldots m_n\, i_1 i_2\ldots i_X} = (-1)^{m_1+m_2+\cdots+m_n}\xi_{m_1}\xi_{m_2}\cdots\xi_{m_n}\xi^{1/2}_{i_1}\xi^{1/2}_{i_2}\cdots\xi^{1/2}_{i_X}, \tag{84}$$

and where $E_{m_1m_2\ldots m_n\, j_1 j_2\ldots j_X}$, which arises from the expansion of the first and the second kind geminals, takes the form

$$\begin{aligned}
E_{m_1m_2\ldots m_n\, j_1 j_2\ldots j_X} = {}& \sum_{P\subset S_n} P(m_1, m_2, \ldots, m_n)\big(A_{j_1}\delta_{j_1,m_1} + \Delta(m_1 - j_1)B_{j_1}\big) \\
& \times\big(A_{j_2}\delta_{j_2,m_2} + \Delta(m_2 - j_2)B_{j_2}\big)\cdots\big(A_{j_y}\delta_{j_y,m_y} + \Delta(m_y - j_y)B_{j_y}\big)
\end{aligned} \tag{85}$$

with

$$\Delta(m_i, j_i) = \begin{cases} 1, & m_i > j_i, \\ 0, & m_i \leqslant j_i, \end{cases} \tag{86}$$

in which $\{P(m_1, m_2, \ldots, m_n)\}$ are used to denote the elements of the permutation group S_n and they permute the indices $(m_1, m_2, \ldots, m_n)$ in equation (83). Notice that for a given basis $|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle$ in equation (42) the indices $(j_1, j_2, \ldots, j_y)$ and $(i_1, i_2, \ldots, i_X)$ are fixed, and they satisfy the same relations given by equations (54)–(56). The indices $(m_1, m_2, \ldots, m_n)$ in the summation in equation (83) take the values in the range

$$m_1, m_2, \ldots, m_n = 1, 2, \ldots, M, \quad 1 \leqslant m_1 < m_2 < \cdots < m_n \leqslant M. \tag{87}$$

Furthermore, the running indices $(m_1, m_2, \ldots, m_n)$ and the fixed indices $(j_1, j_2, \ldots, j_y)$ and $(i_1, i_2, \ldots, i_X)$ are subjected to the relations

$$m_{z+1} \geqslant j_1,\ m_{z+2} \geqslant j_2, \ldots,\ m_n \geqslant j_y,\ z = (N - V_1)/2, \tag{88}$$

$$(m_1, m_2, \ldots, m_n) \cap (i_1, i_2, \ldots, i_X) = \emptyset \quad \text{(empty set)}. \tag{89}$$

From equations (76) and (83), it is easy to express

$$\left\langle \left[(\alpha_M)\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\right]\right|$$

in the form

$$\begin{aligned}
&\left\langle \left[(\alpha_M)\langle 1^{V_M}\rangle \cdots (\alpha_2)\langle 1^{V_2}\rangle(\alpha_1)\langle 1^{V_1}\rangle N\right]\right| \\
&= C(M,N,V_1)\langle 0|(Q^+)^{n-y}\prod_{L=1}^{y}(G(j_L, V_{j_L+1}))^+\prod_{k=1}^{X}(a^+_{i_k(\alpha_{i_k})}(\xi_{i_k}))^+ \\
&= C(M,N,V_1)\langle 0|\sum_{m_1,m_2,\ldots,m_n} D^*_{m_1m_2\ldots m_n\, i_1i_2\ldots i_X} E_{m_1m_2\ldots m_n\, j_1j_2\ldots j_y} \\
&\quad \times b_{m_n}\cdots b_{m_2}b_{m_1}a_{i_X(\alpha_{i_X})}\cdots a_{i_2(\alpha_{i_2})}a_{i_1(\alpha_{i_1})},
\end{aligned} \tag{90}$$

where

$$D^*_{m_1m_2\ldots m_n\, i_1i_2\ldots i_X} = (-1)^{m_1+m_2+\cdots+m_n}\xi^*_{m_1}\xi^*_{m_2}\cdots\xi^*_{m_n}\xi^{*\,1/2}_{i_1}\xi^{*\,1/2}_{i_2}\cdots\xi^{*\,1/2}_{i_X}. \tag{91}$$

Notice that Q^+, $(a^+_{i_k(\alpha_{i_k})}(\xi_{i_k}))^+$ and $(G(j_L, V_{j_L+1}))^+$ in equation (90) are given by equations (77) and (78).

For illustration, AGP and GSPG for $Sp(8)$ with $M = 4$ and $N = 4$ are taken as examples.

For AGP, we have

$$\begin{aligned}
&\left|4\langle 0\rangle(0)\langle 0\rangle(0)\langle 0\rangle(0)\langle 0\rangle(0)\right\rangle = \frac{1}{\sqrt{4!}}Q^2|0\rangle \\
&= \frac{1}{\sqrt{24}}\big(-\xi_1\xi_2b_1^+b_2^+ + \xi_1\xi_3b_1^+b_3^+ - \xi_1\xi_4b_1^+b_4^+ - \xi_2\xi_3b_2^+b_3^+ \\
&\qquad + \xi_2\xi_4b_2^+b_4^+ - \xi_3\xi_4b_3^+b_4^+\big)|0\rangle,
\end{aligned}$$

$$\begin{aligned}
&\left\langle\left[(0)\langle 0\rangle(0)\langle 0\rangle(0)\langle 0\rangle(0)\langle 0\rangle 4\right]\right| = \frac{1}{\sqrt{4!}}\langle 0|(Q^+)^2 \\
&= \frac{1}{\sqrt{24}}\langle 0|\big(-\xi_1^*\xi_2^*b_2b_1 + \xi_1^*\xi_3^*b_3b_1 - \xi_1^*\xi_4^*b_4b_1 - \xi_2^*\xi_3^*b_3b_2 \\
&\qquad + \xi_2^*\xi_4^*b_4b_2 - \xi_3^*\xi_4^*b_4b_3\big).
\end{aligned}$$

This AGP possesses double and quadruple excitations.

For GSPG, we have

$$\begin{aligned}
&\left|4\langle 1^4\rangle(1)\langle 1^3\rangle(0)\langle 1\rangle(1)\langle 0\rangle(0)\right\rangle = G(2,1)a_1^+(\xi_1)a_3^+(\xi_3)|0\rangle \\
&= \frac{1}{\sqrt{2}}\big(\xi_2\xi_1^{1/2}\xi_3^{1/2}b_2^+a_1^+a_3^+ - \xi_4\xi_1^{1/2}\xi_3^{1/2}b_4^+a_1^+a_3^+\big)|0\rangle,
\end{aligned}$$

$$\left\langle \left[(0)\langle 0\rangle(1)\langle 1\rangle(0)\langle 1^3\rangle(1)\langle 1^4\rangle 4\right]\right| = \langle 0|(G(2,1))^+ a_3(\xi_3)a_1(\xi_1)$$
$$= \frac{1}{\sqrt{2}}\langle 0|\left(\xi_2^*\xi_1^{*\,1/2}\xi_3^{*\,1/2}b_2a_3a_1 - \xi_4^*\xi_1^{*\,1/2}\xi_3^{*\,1/2}b_4a_3a_1\right).$$

This GSPG possesses single and triple excitations.

Furthermore, for a given basis $|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle$, a quantity R is defined as

$$R = \sum_{i=1}^{t}|\alpha_i|, \quad t = \begin{cases} N/2, & \text{for even } N, \\ (N+1)/2, & \text{for odd } N. \end{cases} \tag{92}$$

When R is an even(odd) number for even N, the basis possesses even(odd)-fold excitations, whereas when R is an even(odd) number for odd N, the basis possesses odd(even)-fold excitations.

6. On the spin of the symplectic basis set

Since the spin s and its component m_s either for the first or for the second kind geminals are equal to zero, the total spin S and its component M_s for a given basis $|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle$ are only determined by the one-particle operators $a^+_{i_1(\alpha_{i_1})}a^+_{i_2(\alpha_{i_2})}\cdots a^+_{i_X(\alpha_{i_X})}$, and it is obvious, from $\alpha = 1$ and $\alpha = -1$ which correspond to spin up and spin down, that

$$M_s = \frac{1}{2}\sum_{k=1}^{X}\alpha_{i_k} = \frac{1}{2}\sum_{i=1}^{M}\alpha_i. \tag{93}$$

In the second expression, we have made use of that there are, except $(\alpha_{i_1}, \alpha_{i_2}, \ldots, \alpha_{i_X})$, $M - X$ components of the weight $(\alpha_1, \alpha_2, \ldots, \alpha_M)$ equal to zero.

By means of the symplectic bases $\{|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle\}$ given by equation (51) which possess the same part of

$$C(M,N,V_1)Q^{(N-V_1)/2}\prod_{L=1}^{(V_1-X)/2}G(j_L, V_{j_L+1}),$$

we can make use of the parts

$$\prod_{k=1}^{X}a^+_{i_k(\alpha_{i_k})},$$

in which the components $(\alpha_{i_1}, \alpha_{i_2}, \ldots, \alpha_{i_X})$ take the values in the range $(\pm 1, \pm 1, \ldots, \pm 1)$, to construct the bases with definite total spin S together with $M_s = S, S-1, \ldots, -S$. Alternatively, when we choose the symplectic bases $\{|N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle\}$ in which the symplectic numbers $(V_1, V_2, \ldots, V_M)$ are fixed and the X non-zero components of the weight $(\alpha_1, \alpha_2, \ldots, \alpha_M)$ take the values 1 or -1, we can construct the bases with definite total spin S together with $M = S, S-1, \ldots, -S$.

For illustration, the four GSPG of $Sp(8)$ with $M = 4$ and $N = 4$

$$\left|4\langle 1^4\rangle(0)\langle 1^2\rangle(\pm 1)\langle 1\rangle(\pm 1)\langle 0\rangle(0)\right\rangle = G(1,2)a^+_{2(\pm 1)}(\xi_2)a^+_{3(\pm 1)}(\xi_3)|0\rangle$$

are taken as an example such that

$$\begin{aligned}
&\left|\psi\ (S=0, M_S=0)\right\rangle \\
&\quad = \frac{1}{\sqrt{2}}\left(\left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(1)\,\langle 1\rangle(-1)\,\langle 0\rangle(0)\right\rangle - \left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(-1)\,\langle 1\rangle(1)\,\langle 0\rangle(0)\right\rangle\right) \\
&\quad = \frac{1}{\sqrt{2}}G(1,2)\left(a^+_{\bar{2}}(\xi_2)a^+_{\bar{3}}(\xi_3) - a^+_{\bar{2}}(\xi_2)a^+_{3}(\xi_3)\right)|0\rangle,
\end{aligned}$$

$$\begin{aligned}
\left|\psi\ (S=1, M_S=1)\right\rangle &= \left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(1)\,\langle 1\rangle(1)\,\langle 0\rangle(0)\right\rangle \\
&= G(1,2)a^+_2(\xi_2)a^+_3(\xi_3)|0\rangle,
\end{aligned}$$

$$\begin{aligned}
&\left|\psi\ (S=1, M_S=0)\right\rangle \\
&\quad = \frac{1}{\sqrt{2}}\left(\left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(1)\,\langle 1\rangle(-1)\,\langle 0\rangle(0)\right\rangle + \left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(-1)\,\langle 1\rangle(1)\,\langle 0\rangle(0)\right\rangle\right) \\
&\quad = \frac{1}{\sqrt{2}}G(1,2)\left(a^+_2(\xi_2)a^+_{\bar{3}}(\xi_3) + a^+_{\bar{2}}(\xi_2)a^+_3(\xi_3)\right)|0\rangle,
\end{aligned}$$

$$\begin{aligned}
\left|\psi\ (S=1, M_S=-1)\right\rangle &= \left|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(-1)\,\langle 1\rangle(-1)\,\langle 0\rangle(0)\right\rangle \\
&= G(1,2)a^+_{\bar{2}}(\xi_2)a^+_{\bar{3}}(\xi_3)|0\rangle.
\end{aligned}$$

7. On the optimization calculations of LiH molecule with respect to AGP, SPG and AGP-SPG

For a system with N electrons, we choose $2M$ spin-orbitals which are taken from the Hartree–Fock procedure as starting point, and also we choose appropriately the state vector $|\psi\rangle$ as a linear sum of a number of symplectic bases, i.e.,

$$\begin{aligned}
|\psi\rangle = \sum_{\{V_i,\alpha_i\}} & C\left(\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\right) \\
& \times |N\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\rangle,
\end{aligned} \tag{94}$$

in which the symplectic bases can be further expressed in terms of the Slater determinants given by equation (83). The optimization procedure for solving Schrödinger equation by variation method is extended to the coefficients

$$\left\{C\left(\langle 1^{V_1}\rangle(\alpha_1)\,\langle 1^{V_2}\rangle(\alpha_2)\cdots\langle 1^{V_M}\rangle(\alpha_M)\right)\right\},$$

the geminal coefficients $\{\xi_1\xi_2\cdots\xi_M\}$ [6,13], and the orbitals $\{a_1^+|0\rangle, a_2^+|0\rangle, \ldots, a_M^+|0\rangle\}$ [26,27].

It is known that by means of AGP, LiH molecule was investigated by using 13-CGTO basis [21] and it was shown that the AGP basis led to the calculated energies associated with high percentage of correlation energy. In this section, we only give a brief discussion on the calculations of LiH molecule with respect to AGP, SPG and AGP-SPG. The STO-6G molecular orbitals of Gaussian 94 program are taken as the starting point, and the numerical values of the one-center and two-center integrals are taken from the same program. In this paper, the choice of STO-6G basis set is not for the accurate calculations, but rather for the exhibition of some important properties of the symplectic bases.

From the expansion of the symplectic bases as a linear sum of Slater determinants in equation (83), it is not difficult to find that the AGP, SPG and AGP-SPG bases are expressible in terms of the same types of the Slater determinants, but with different coefficients. Since the STO-6G is associated with $Sp(12)$, we have

$$|\mathrm{AGP}\rangle = \big|4\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\big\rangle = \sum_{1\leqslant i<j\leqslant 6} A_{ij} a_i^+ a_{\bar{i}}^+ a_j^+ a_{\bar{j}}^+|0\rangle,$$

where

$$A_{ij} = (-1)^{i+j}\xi_i\xi_j a_{ij} \tag{95}$$

with

$$a_{12} = a_{13} = a_{14} = a_{15} = a_{16} = a_{23} = a_{24} = a_{25} = a_{26} = a_{34} = a_{35} = a_{36} = a_{45} = a_{46} = a_{56} = \frac{1}{\sqrt{15}},$$

$$|\mathrm{SPG}\rangle = \big|4\langle 1^4\rangle(0)\,\langle 1^2\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\big\rangle = \sum_{1\leqslant i<j\leqslant 6} B_{ij} a_i^+ a_{\bar{i}}^+ a_j^+ a_{\bar{j}}^+|0\rangle,$$

where

$$B_{ij} = (-1)^{i+j}\xi_i\xi_j b_{ij} \tag{96}$$

with

$$b_{12} = \sqrt{\tfrac{3}{5}},\ b_{13} = b_{14} = b_{15} = b_{16} = b_{23} = b_{24} = b_{25} = b_{26} = -\tfrac{1}{4}\sqrt{\tfrac{3}{5}},$$
$$b_{34} = b_{35} = b_{36} = b_{45} = b_{46} = b_{56} = \tfrac{1}{6}\sqrt{\tfrac{3}{5}},$$

$$\big|(\mathrm{AGP}-\mathrm{SPG})_1\big\rangle = \big|4\langle 1^2\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\big\rangle$$

$$= \sum_{1\leqslant i<j\leqslant 6} C_{ij} a_i^+ a_{\bar{i}}^+ a_j^+ a_{\bar{j}}^+ |0\rangle,$$

where

$$C_{ij} = (-1)^{i+j} \xi_i \xi_j c_{ij} \tag{97}$$

with

$$c_{12} = c_{13} = c_{14} = c_{15} = c_{16} = \sqrt{\tfrac{2}{15}},$$
$$c_{23} = c_{24} = c_{25} = c_{26} = c_{34} = c_{35} = c_{36} = c_{45} = c_{46} = c_{56} = -\sqrt{\tfrac{1}{30}},$$

$$\big|(\text{AGP} - \text{SPG})_2\big\rangle = \big|4\langle 1^2\rangle(0)\,\langle 1^2\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\,\langle 0\rangle(0)\big\rangle$$
$$= \sum_{1\leqslant i<j\leqslant 6} D_{ij} a_i^+ a_{\bar{i}}^+ a_j^+ a_{\bar{j}}^+ |0\rangle,$$

where

$$D_{ij} = (-1)^{i+j} \xi_i \xi_j d_{ij} \tag{98}$$

with

$$d_{12} = \sqrt{\tfrac{1}{5}},\ d_{13} = d_{14} = d_{15} = d_{16} = -\tfrac{1}{4}\sqrt{\tfrac{1}{5}},$$
$$d_{23} = d_{24} = d_{25} = d_{26} = \tfrac{3}{4}\sqrt{\tfrac{1}{5}}, d_{34} = d_{35} = d_{36} = d_{45} = d_{46} = d_{56} = -\tfrac{1}{2}\sqrt{\tfrac{1}{5}}.$$

Since the AGP, SPG, $(\text{AGP-SPG})_1$ and $(\text{AGP-SPG})_2$ are expanded in terms of the same types of the Slater determinants, these four symplectic bases lead, via the optimizations of the orbitals and the geminal parameters $\{\xi_i\}$, to the same calculated energies

$$E(\text{AGP}) = E(\text{SPG}) = E\big((\text{AGP} - \text{SPG})_1\big) = E\big((\text{AGP} - \text{SPG})_2\big). \tag{99}$$

These calculated results are listed in table 1 with respect to different internuclear distance. Notice that though the optimization results of the geminal parameters are different with respect to AGP, SPG, $(\text{AGP-SPG})_1$ and $(\text{AGP-SPG})_2$ as shown in table 2, the calculated coefficients A_{ij}, B_{ij}, C_{ij} and D_{ij} in equations (95)–(98) are nearly the same as listed in table 3. The calculated results of the AGP, SPG, $(\text{AGP-SPG})_1$ and $(\text{AGP-SPG})_2$ bases for LiH which possess the same high percentage of correlation energy are omitted.

Furthermore, when the state is chosen as a linear sum of the AGP, SPG, $(\text{AGP-SPG})_1$ and $(\text{AGP-SPG})_2$, i.e.,

$$|\psi\rangle = C_1|\text{AGP}\rangle + C_2|\text{SPG}\rangle + C_3|(\text{AGP} - \text{SPG})_1\rangle + C_4|(\text{AGP} - \text{SPG})_2\rangle, \tag{100}$$

we obtain, via the optimizations of the orbitals, the geminal parameters $\{\xi_i\}$ and the coefficients $\{C_i\}$, the calculated energies for LiH molecule which are the same as those calculated results by using AGP, SPG, $(\text{AGP-SPG})_1$ and $(\text{AGP-SPG})_2$ listed in table 1.

Table 1
The calculated energies (a.u.) of LiH with respect to different internuclear distance R.

R(bohr)	AGP	SPG	(AGP-SPG)$_1$	(AGP-SPG)$_2$	AGP[a]
2.000	–7.901277	–7.901277	–7.901277	–7.901278	–7.88039
3.015[b]	–7.972140	–7.972140	–7.972140	–7.972141	–7.97516
4.000	–7.941202	–7.941203	–7.941202	–7.941203	–7.96379
6.000	–7.882247	–7.882248	–7.882247	–7.882248	–7.92596
8.000	–7.872031	–7.872031	–7.872031	–7.872031	–7.91108
10.00	–7.871054	–7.871054	–7.871054	–7.871054	–7.90895
20.00	–7.870964	–7.870964	–7.870964	–7.870964	–7.90859

[a] Due to Öhrn et al. [21], with basis (7s2p).
[b] $R = 3.015$ is the equilibrium internuclear distance of LiH.

Table 2
The optimized geminal parameters $\{|\xi_i|\}$[a] of AGP, SPG, (AGP-SPG)$_1$ and (AGP-SPG)$_2$ at $R = 3.015$ bohr.

$\lvert\xi_i\rvert$	AGP	SPG	(AGP-SPG)$_1$	(AGP-SPG)$_2$
$\lvert\xi_1\rvert$	9.9985×10^{-1}	9.9980×10^{-1}	9.9941×10^{-1}	9.9998×10^{-1}
$\lvert\xi_2\rvert$	1.6925×10^{-2}	1.6989×10^{-2}	3.3875×10^{-2}	5.6653×10^{-3}
$\lvert\xi_3\rvert$	6.8562×10^{-5}	2.7616×10^{-4}	1.3724×10^{-4}	9.2094×10^{-5}
$\lvert\xi_4\rvert$	4.6218×10^{-4}	1.8561×10^{-3}	9.2502×10^{-4}	6.1893×10^{-4}
$\lvert\xi_5\rvert$	4.6218×10^{-4}	1.8561×10^{-3}	9.2502×10^{-4}	6.1893×10^{-4}
$\lvert\xi_6\rvert$	2.4665×10^{-3}	9.9036×10^{-3}	4.9365×10^{-3}	3.3025×10^{-3}

[a] $|\xi_i| = (\xi_i \xi_i^*)^{1/2}$ is the modulus of the geminal coefficient ξ_i.

Table 3
The optimization coefficients $A_{ij}, B_{ij}, C_{ij}, D_{ij}$ for AGP, SPG, (AGP-SPG)$_1$ and (AGP-SPG)$_2$ at $R =$ 3.015 bohr.

$(i\ j)$[a]	A_{ij}	B_{ij}	C_{ij}	D_{ij}
(1 2)	0.988815	0.988814	−0.988815	−0.988814
(1 3)	−0.004006	−0.004018	0.004006	0.004018
(1 4)	−0.027002	−0.027007	0.027002	0.027007
(1 5)	−0.027002	−0.027007	0.027002	0.027007
(1 6)	−0.144100	−0.144102	0.144099	0.144102
(2 3)	−0.000068	−0.000068	0.000068	0.000068
(2 4)	−0.000457	−0.000459	0.000458	0.000459
(2 5)	−0.000457	−0.000459	0.000458	0.000459
(2 6)	−0.002439	−0.002449	0.002442	0.002449
(3 4)	0.000002	0.000005	−0.000002	−0.000005
(3 5)	0.000002	0.000005	−0.000002	−0.000005
(3 6)	0.000010	0.000027	−0.000010	−0.000027
(4 5)	0.000012	0.000033	−0.000012	−0.000033
(4 6)	0.000067	0.000178	−0.000067	−0.000178
(5 6)	0.000067	0.000178	−0.000067	−0.000178

[a] The symbol (i, j) is used to denote the coefficients A_{ij}, B_{ij}, C_{ij} and D_{ij} in equations (95)–(98) with respect to AGP, SPG, (AGP-SPG)$_1$ and (AGP-SPG)$_2$ bases.

For brevity, the details are omitted here. When we consider more symplectic bases in the linear sum in equation (42) in the calculation of LiH molecule with STO-6G, we find that the contribution of AGP, SPG, $(\text{AGP-SPG})_1$ and $(\text{AGP-SPG})_2$ are not the same, and the effect of the geminals with non-linear variation parameters reduce, in comparison with the extreme symplectic bases ($\xi_i = 1$), a great number of the symplectic bases ($\xi_i \neq 1$) in the variation procedure. These primary calculated results need to be further verified by use of larger basis set than STO-6G, in this paper, we do not go further into these details.

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