An efficient approach to CI: General matrix element formulas for spin-coupled particle–hole excitations

Paul Tavan[a] and Klaus Schulten

Max-Planck-Institut für biophysikalische Chemie, Abteilung für Spektroskopie, D-3400 Göttingen, Federal Republic of Germany

(Received 27 August 1979; accepted 22 October 1979)

A new, efficient algorithm for the evaluation of the matrix elements of the CI Hamiltonian in the basis of spin-coupled ν-fold excitations (over orthonormal orbitals) is developed for even electron systems. For this purpose we construct an orthonormal, spin-adapted CI basis in the framework of second quantization. As a prerequisite, spin and space parts of the fermion operators have to be separated; this makes it possible to introduce the representation theory of the permutation group. The ν-fold excitation operators are Serber spin-coupled products of particle–hole excitations. This construction is also designed for CI calculations from multireference (open-shell) states. The $2N$-electron Hamiltonian is expanded in terms of spin-coupled particle–hole operators which map any ν-fold excitation on ν-, $\nu\pm1$-, and $\nu\pm2$-fold excitations. For the calculation of the CI matrix this leaves one with only the evaluation of overlap matrix elements between spin-coupled excitations. This leads to a set of ten general matrix element formulas which contain Serber representation matrices of the permutation group $S^\nu\times S^\nu$ as parameters. Because of the Serber structure of the CI basis these group-theoretical parameters are kept to a minimum such that they can be stored readily in the central memory of a computer for $\nu\leq4$ and even for higher excitations. As the computational effort required to obtain the CI matrix elements from the general formulas is very small, the algorithm presented appears to constitute for even electron systems a promising alternative to existing CI methods for multiply excited configurations, e.g., the unitary group approach. Our method makes possible the adaptation of spatial symmetries and the selection of any subset of configurations. The algorithm has been implemented in a computer program and tested extensively for $\nu\leq4$ and singlet ground and excited states.

I. INTRODUCTION

A. Efficiency of CI methods

The main difficulties arising in quantum chemical configuration interaction (CI) calculations of electronic states in atoms and molecules originate from the large size of the configuration space necessary for sufficiently accurate descriptions. Enormous efforts have been invested to develop numerically efficient algorithms for the solution of the CI problem. In the following we present an algorithm for the evaluation of the CI Hamiltonian which we found very efficient in numerical applications.

Most commonly quantum chemical CI calculations are performed for a spin-independent Hamiltonian $\hat{H}$. Hence, we will assume $\hat{H}$ to commute with the total electronic spin operators $\hat{\mathbf{S}}^2$ and $\hat{S}_z$. A considerable reduction of the size of the CI expansion of the electronic wave function can then be achieved by chosing for a basis eigenfunctions of $\hat{\mathbf{S}}^2$ and $\hat{S}_z$ (spin-adapted linear combinations of Slater determinants).

One can express the elements of the Hamiltonian matrix as weighted sums of spatial one- and two-electron integrals (see for example Ref. 1)

$$\langle\Psi_a|\hat{H}|\Psi_b\rangle=\sum_{i,j}C^{ab}_{ij}F_{ij}+\sum_{i,j,k,l}C^{ab}_{ijkl}(ij|kl)\quad.\qquad(1.1)$$

The weights C^{ab}_{ij} and C^{ab}_{ijkl} are obtained by integrating the various spin-coupled basis functions Ψ_a and Ψ_b over the N spin coordinates as well as the N-1 and N-2 spatial coordinates. In case the N electron functions are constructed from orthonormal molecular orbitals, the weights C^{ab}_{ij} and C^{ab}_{ijkl} are determined entirely by the permutational symmetry of the functions Ψ_a and Ψ_b. For the construction of the "most efficient" CI method one would proceed as follows:

(i) one determines all types of formulas (1.1) needed;

(ii) one provides a numerical program for the evaluation of matrix elements with access to all formulas (1.1) stored in the central memory of the computer.

The direct calculation of the formulas (1.1) (e.g., by means of the "Slater–Condon rules"[2–4]) presents no serious difficulties as long as only singlet or triplet configurations containing a small number of open shells (e.g., single or double excitations of a closed shell Hartree–Fock determinant) are taken into account.[5–11] Furthermore, the number of such formulas is so small, that they can be stored easily in the core of a computer. Several implementations of the "most efficient" CI method for these cases, even avoiding to set up the CI matrix explicitly (see Ref. 12 and references quoted therein), have been developed.

However, if configurations of higher multiplicity containing a larger number of open shells are to be included in the CI expansion, as is necessary for example for the calculation of excited states, one is limited by the rapidly increasing number of formulas for the different types of matrix elements (1.1). In this case, direct calculation of these formulas is very cumbersome and their storage in the central memory of a computer becomes impossible. Group theoretical methods[13–17] or Lie-algebra techniques[1,18–26] are then employed to generate the

[a]Now at the Institut für Physikalische Chemie und Quantenchemie, Freie Universitat Berlin, FB 21/WE 3, Takustr. 3, 1000 Berlin 33.

 0021-9606/80/063547-30$01.00

weights in (1.1) numerically. The computational effort required can be reduced if one rather generates the weights from a smaller number of general matrix element formulas. These general formulas contain a set of parameters (e.g., elements of permutation matrices,[1,13-17] Sanibel coefficients,[27] etc.) which depend on the occupancy pattern, spin coupling and orbital arrangement of the configurations Ψ_a and Ψ_b, i.e., on their permutational symmetry. For the generation of the matrix elements (1.1) from the general formulas the proper values of these parameters have to be determined and then the weights C have to be calculated. Consequently the efficiency of a CI method is determined by the amount of computational work which has to be done at this step.

In this paper we develop a new "very efficient" CI method for molecular systems containing an even number of $N=2N_h$ electrons. In the particle–hole formalism of second quantization we construct an orthonormal spin-coupled CI basis from a closed-shell reference determinant by Serber spin-coupled ν-fold excitation operators. These operators are represented as ν-fold spin-coupled products of single excitations (Sec. III). This representation is particularly designed for CI calculations on multireference (open shell) states constructing the latter as a superposition of excitations from a closed shell reference determinant.

It is shown in Sec. IV how the commutators of the Hamiltonian and the ν-fold excitation operators can be represented as linear combinations of ν-, $(\nu\pm1)$-, and $(\nu\pm2)$-fold excitation operators. This reduces the calculation of the Hamiltonian matrix elements to the calculation of scalar products of spin-coupled ν-fold excitations. An analysis of these scalar products leads to a set of ten general matrix element formulas from which all possible matrix elements (1.1) can be generated easily. Extended PPP–CI studies on the excited states of polyenes[28] and polyacenes,[29] including up to all quadruple excitations, demonstrated the efficiency of our method.

In the derivation of these formulas we show, quite analogously to the usual procedure with many particle functions (see for example Ref. 17), how to separate the spin- and space-parts of the Fermion operators of second quantization. As a consequence we are able to employ the representation theory of the symmetric group for the calculation of matrix elements and of products of spin-coupled excitation operators (Sec. II). It is this last feature which allows the development of a new "CI" method which constructs excited states from a multiconfigurational ground state rather than from a closed shell single configurational ground state.[30] This method is a generalization of the "renormalized CI method" proposed by Ohmine *et al.*[31] for the PPP description of excited polyene states and will be described in a future publication.

The parameters appearing in our general matrix element formulas belong to a subset of the set of all elements of the Serber representation matrices of the subgroup $S^\nu \times S^\nu$ of the permutation group $S^{2\nu}$ of 2ν objects (ν is the upper limit of the degree of excitation of the configurations considered). As long as only configurations containing up to eight open shells are included in the CI expansion this set is small enough that it can be stored easily in the core of a computer. Furthermore, only very little computational work is needed to create the weights C in (1.1) from the parameters (e.g., for matrix elements of ν-fold excitations containing 2ν open shells the Serber matrix elements are identical with the weights). We will also point out possibilities for a reduction of the length of the parameter list so that the latter could be stored in the central memory for even more than eight open shell configurations. But since any such reduction leads to an increase of computational work for the weight generation we did not follow this line of investigation very far (Sec. V). The significant advance of our CI method over previous treatments employing similar matrix element formulas[13-16] is due to the reduced size of our parameter list (see below). This reduction is a result of the particle–hole coupling of the ν-fold excitation operators and of the structure of the pertinent Serber representation matrices (Appendix I).

In the remainder of this section we will define the physical problem, comment briefly on previous solutions and introduce part of our notation.

B. Definition of the physical problem

We consider a system of N electrons in the Coulomb potential of fixed nuclei. N is assumed to be even ($N=2N_h$). Neglecting magnetic and relativistic effects the Hamiltonian is

$$\hat{H}=\hat{Z}+\hat{V} \tag{1.2a}$$

$$\hat{Z}=\sum_i \hat{z}_i \tag{1.2b}$$

$$\hat{V}=\sum_{i<j} \hat{v}_{ij} \ . \tag{1.2c}$$

$\hat{z}_i$ represents the one-particle operator corresponding to the kinetic energy of the ith electron and its potential energy in the field of the nuclei and $\hat{v}_{ij}$ represents the two-particle operator accounting for the Coulomb repulsion between electrons i and j. One seeks approximate solutions of the time-independent Schrödinger equation

$$\hat{H}\left|\Psi_\tau^N\right\rangle = E_\tau \left|\Psi_\tau^N\right\rangle \qquad \tau=0,1,2,\ldots \tag{1.3}$$

for the energetically lowest eigenstates of the system. For this purpose we expand these states in a suitable N electron basis $\{|k\rangle \mid k=1,2,\ldots\}$

$$\left|\Psi_\tau^N\right\rangle = \sum_k c_{\tau k}|k\rangle \ . \tag{1.4}$$

Equation (1.3) is thereby transformed to a generalized matrix eigenvalue problem. If the basis is orthonormal (ON), (1.3) is reduced to the ordinary matrix eigenvalue problem

$$\sum_k c_{\tau k} H_{k'k} = E_\tau c_{\tau k'} \ . \tag{1.5}$$

We call a basis "suitable" if it is ON and if its elements have all the symmetry properties of the exact solutions $|\Psi_\tau^N\rangle$.

C. Symmetries of the Hamiltonian and properties of its eigenfunctions

$\hat{H}$ contains no spin terms and consequently commutes with the total electronic spin operator $\hat{\mathbf{S}}$

$$\hat{\mathbf{S}}=\sum_i \hat{\boldsymbol{\sigma}}_i \tag{1.6}$$

$$[\hat{H},\hat{\mathbf{S}}]=0 \ . \tag{1.7}$$

Therefore, the eigenfunctions $|\Psi_\tau^N\rangle$ of $\hat{H}$ are also eigenfunctions of $\hat{\mathbf{S}}^2$ and $\hat{S}_z$

$$\hat{\mathbf{S}}^2\left|\Psi_{\tau,S,M}^N\right\rangle=S(S+1)\left|\Psi_{\tau,S,M}^N\right\rangle \ , \tag{1.8a}$$

$$\hat{S}_z\left|\Psi_{\tau,S,M}^N\right\rangle=M\left|\Psi_{\tau,S,M}^N\right\rangle \ . \tag{1.8b}$$

Let S^N denote the permutation group of N objects and $\hat{P}$ denote the unitary operator which causes a simultaneous permutation p^{-1} of the spatial coordinates $\mathbf{x}_1,\ldots,\mathbf{x}_N$ and of the spin coordinates $\sigma_1,\ldots,\sigma_N$ in the wave function $|\Psi_\tau^N\rangle$. The operators $\hat{P}$ form an operator representation $\hat{S}^N$ of the elements p of the permutation group S^N(cf. Ref. 32, p. 105). Because of the identity of the electrons one has

$$[\hat{H},\hat{P}]=[\hat{\mathbf{S}}^2,\hat{P}]=[\hat{S}_z,\hat{P}]=0 \ . \tag{1.9}$$

Thus, the eigenfunctions $|\Psi_{\tau,S,M}^N\rangle$ span a representation of S^N. According to the Pauli principle, this is the totally antisymmetric representation

$$\hat{P}\left|\Psi_{\tau,S,M}^N\right\rangle=\epsilon(p)\left|\Psi_{\tau,S,M}^N\right\rangle \ , \tag{1.10}$$

where $\epsilon(p)$ is the signature of the permutation p represented by the operator $\hat{P}$.

It is appropriate to decompose $\hat{P}$ into a spatial and a spin part

$$\hat{P}=\hat{P}^r\hat{P}^\sigma=\hat{P}^\sigma\hat{P}^r \ . \tag{1.11}$$

$\hat{P}^r$ is to permute solely the spatial coordinates and $\hat{P}^\sigma$ is to permute solely the spin coordinates. According to (1.7) $\hat{H}$ is totally symmetric with respect to all permutations of the spatial coordinates alone

$$[\hat{H},\hat{P}^r]=0 \ . \tag{1.12}$$

Likewise, $\hat{\mathbf{S}}^2$ and $\hat{S}_z$ are invariant under similarity transformations which permute solely the spin coordinates

$$[\hat{\mathbf{S}}^2,\hat{P}^\sigma]=[\hat{S}_z,\hat{P}^\sigma]=0 \ . \tag{1.13}$$

Therefore, one can represent the eigenfunctions $|\Psi_{\tau,S,M}^N\rangle$ as linear combinations of products of spatial functions $|\Phi_{\tau,S,k}^N\rangle$ and spin functions $|\Theta_{S,M,k}^N\rangle$, $k=1,2\ldots,f_S^N$ which separately span irreducible representations of the symmetric group

$$\left|\Psi_{\tau,S,M}^N\right\rangle=\frac{1}{\sqrt{f_S^N}}\sum_{k=1}^{f_S^N}\left|\Phi_{\tau,S,k}^N\right\rangle\left|\Theta_{S,M,k}^N\right\rangle \ . \tag{1.14}$$

The corresponding representation matrices of the irreducible representation $[\frac{1}{2}N+S,\frac{1}{2}N-S]$ of the permutation group

$$U_{lk}^{SN}(p)=\langle\Phi_{\tau,S,l}^N\left|\hat{P}^r\right|\Phi_{\tau,S,k}^N\rangle \tag{1.15}$$

can be assumed to be orthogonal and real. Their dimension f_S^N is

$$f_S^N=\frac{(2S+1)N!}{(\frac{1}{2}N+S+1)!\,(\frac{1}{2}N-S)!} \ . \tag{1.16}$$

For any permutation p of S^N we have

$$\hat{P}^r\left|\Phi_{\tau,S,k}^N\right\rangle=\sum_{l=1}^{f_S^N}U_{lk}^{SN}(p)\left|\Phi_{\tau,S,l}^N\right\rangle \ . \tag{1.17}$$

The functions $|\Phi_{\tau,S,k}^N\rangle$ of the spatial coordinates are eigenfunctions of the Hamiltonian which one can assume to be orthonormal:

$$\hat{H}\left|\Phi_{\tau,S,k}^N\right\rangle=E_\tau\left|\Phi_{\tau,S,k}^N\right\rangle \quad k=1,\ldots,f_S^N \tag{1.18}$$

$$\langle\Phi_{\tau,S,k}^N\left|\Phi_{\tau,S,l}^N\right\rangle=\delta_{k,l} \ . \tag{1.19}$$

The spin functions $|\Theta_{S,M,k}^N\rangle$ are ON eigenfunctions of the spin operators $\hat{\mathbf{S}}^2$ and $\hat{S}_z$. Under a permutation $\hat{P}^\sigma$ the spin functions transform irreducibly into linear combinations of each other according to the "dual" representation $\mathbf{V}^{SN}$

$$\hat{P}^\sigma\left|\Theta_{S,M,k}^N\right\rangle=\sum_l V_{lk}^{SN}(p)\left|\Theta_{S,M,l}^N\right\rangle \ . \tag{1.20}$$

To guarantee the antisymmetry (1.10) of the total wave function one has

$$V_{lk}^{SN}(p)=\epsilon(p)U_{lk}^{SN}(p) \ . \tag{1.21}$$

There are many equivalent ways to construct orthonormal spin functions and the corresponding representation matrices. In this paper we will employ the construction of the spin functions due to Serber.[33] Appendix I presents the necessary properties of these functions and of the corresponding Serber representation matrices and introduces several new concepts and theorems.

D. Basis sets for N electron systems

We assume an independent electron Hamiltonian

$$\hat{H}_0=\sum_i(\hat{z}_i+\hat{u}_i) \tag{1.22}$$

as a zero order approximation to the Hamiltonian $\hat{H}$. The $\hat{u}_i$ in (1.22) are Hermitian operators acting on the spatial coordinate of electron i. For the construction of a suitable N electron basis we define the spin orbitals

$$\{|r\sigma\rangle\,|r=1,2\ldots \text{ and } \sigma=\alpha,\beta\} \tag{1.23}$$

as the tensor products

$$|r\sigma\rangle=|\phi_r\rangle|\sigma\rangle \ , \tag{1.23a}$$

where the orbitals $|\phi_r\rangle$ defined by

$$(\hat{z}+\hat{u})\left|\phi_r\right\rangle=\epsilon_r\left|\phi_r\right\rangle \tag{1.23b}$$

form an ON basis of the one-electron space. The spin functions $|\sigma\rangle\in\{|\alpha\rangle,|\beta\rangle\}$ are the eigenfunctions of the one-particle spin operators $\hat{\boldsymbol{\sigma}}^2$ and $\hat{\sigma}_z$

$$\hat{\sigma}_z\left|\alpha\right\rangle=\tfrac{1}{2}\left|\alpha\right\rangle \quad \text{and} \quad \hat{\sigma}_z\left|\beta\right\rangle=-\tfrac{1}{2}\left|\beta\right\rangle \ . \tag{1.23c}$$

1. Slater determinants

The orthonormal and complete basis of Slater determinants is constructed by application of the antisymmetrizer

$$\hat{A}=\frac{1}{N!}\sum_{p\in S^N}\epsilon(p)\hat{P} \tag{1.24}$$

to all N-fold tensor products of N different spin orbitals (1.23)

$$||r_1\ldots r_N\sigma_1\ldots\sigma_N\rangle\rangle=\sqrt{N!}\,\hat{A}|r_1\ldots r_N\sigma_1\ldots\sigma_N\rangle \tag{1.25a}$$

$$|r_1\ldots r_N\sigma_1\ldots\sigma_N\rangle=|r_1\sigma_1\rangle|r_2\sigma_2\rangle\ldots|r_N\sigma_N\rangle\ . \tag{1.25b}$$

In general the resulting *spin orbital configurations* (1.25a) are not eigenfunctions of the total electronic spin operator $\hat{S}^2$. A corresponding CI basis is not "suitable" although the Hamiltonian matrix can easily be calculated by means of the Slater–Condon rules.[2–4]

2. Nonorthogonal basis sets

The oldest approach to the construction of antisymmetric spin-adapted many electron functions, the "VB method," is based on the work of Heitler and Rumer[34] and the related method of Pauling[35] for singlet states. Matsen[36] and Matsen *et al.*[37] proved the equivalence between the Pauling method and the projection of spinfunctions by means of Young operators and generalized this method to arbitrary spin multiplicities. Further generalizations and general matrix element formulas have been derived for these functions by several authors.[38–45]

A second approach originated from Löwdin's proposal[46] to construct spin functions by means of projection operators which are not derived group-theoretically. Harris[27] provided general matrix element formulas for spin-projected determinants composed of orthonormal spin orbitals.

However, since the spin-projected functions as well as the VB functions are nonorthogonal neither represent "suitable" CI basis sets. Furthermore, these functions do not lead to efficient algorithms for the generation of matrix elements from general formulas. For instance, in the case of spin-projected functions a large number of Sanibel coefficients[47–50] have to be calculated for every matrix element.

3. Orthogonal basis sets

Until recently the derivation of useful matrix element formulas seemed to be even more troublesome when the spin-coupled configurations were chosen to be mutually orthogonal. This situation has changed with the work of Ruedenberg *et al.*,[13–15] Kaplan,[17] and Karwowski[16] on one approach to the construction of orthogonal spin-adapted many-electron basis sets and that of Paldus,[20] Segal *et al.*,[22] Ruttink,[1] as well as Shavitt,[23–24] and Brooks and Schaefer[25] on the unitary group approach. The beginning of this work dates back to Dirac's vector model[51] for which Serber[33] had proposed an important modification. Yamanouchi[52] and Kotani *et al.*[53] developed general techniques for orthogonal spin-coupled functions using the theory of the orthogonal representations of the symmetric group (see Ref. 54). For a long time the basic drawback of the Yamanouchi–Kotani–Serber (YKS) method consisted in the lack of efficient matrix element formulas. Complicated sums over the $N!$ elements of the permutation group S^N had to be performed so that only very small systems could be considered. (References to the various applications of the YKS method to atomic, molecular, and nuclear problems can be found in Ref. 14, Ref. 20, and in Kaplan's book.[17])

Ruedenberg, Poshusta, and Salmon[13–15] showed that these sums can be reduced to a few terms if the wave functions are represented as linear combinations of spin-adapted antisymmetrized products (SAAP's) of orthogonal spin orbitals. The SAAP's are given by

$$||r_1\ldots r_N\Theta^N_{S,M,k}\rangle\rangle=C\sqrt{N!}\,\hat{A}(|r_1\ldots r_N\rangle|\Theta^N_{S,M,k}\rangle). \tag{1.26}$$

where C is a normalization constant. The N-fold tensor product $|r_1\ldots r_N\rangle$ (*orbital configuration*) is formed from a suitably ordered set $|\phi_{r_1}\rangle,\ldots,|\phi_{r_N}\rangle$ of spatial orbitals. The spin functions $|\Theta^N_{S,M,k}\rangle$ are coupled according to a certain scheme, e.g., that of Serber (see Appendix I) or that of Yamanouchi and Kotani. The SAAP linear combinations of Slater determinants form an ON basis in the configuration space. The SAAP's can be written in the form (1.14) by means of the $(f^N_S)^2$ spatial functions

$$|r_1\ldots r_N,S,l,k\rangle$$

$$=C\sqrt{\frac{f^N_S}{N!}}\sum_{p\in S^N}U^{S^N}_{lk}(p)\hat{P}^r|r_1\ldots r_N\rangle\ , \tag{1.27}$$

which for every value of k span an irreducible representation of S^N.[17] Consequently the SAAP basis sets are "suitable" for CI calculations.

The general SAAP matrix element formulas derived by Ruedenberg *et al.* in the Serber coupling scheme and by Kaplan[17] in more general coupling schemes are about as simple as the Slater–Condon rules. However, since these expressions contain as parameters for the weight generation (cf. Sec. I A) the elements of the representation matrices $U^{S^N}_{lk}(p)$, they do not lead to efficient CI algorithms for other than very small electronic systems. As the number and dimension of these matrices increase rapidly with the size of the electronic system, the group-theoretical parameters cannot be stored in the central memory of a computer for systems with more than about seven electrons. For instance, for the computation of the singlet states of an eight electron system one would need the 8! representation matrices of S^8 with dimension $f^8_0=14$ entailing together 4 233 600 numbers in symmetrical storage. Thus, the necessary group-theoretical data would have to be recalculated for every matrix element.

To circumvent these difficulties of the SAAP formalism Karwowski[16] derived formulas for the matrix elements of the SAAP's in the Yamanouchi–Kotani (YK) coupling scheme by means of a graphical method. His formulas contain only representation matrices of the permutation group S^{N_o} of the N_o singly occupied orbitals. However, for the same reasons as discussed above even this reduction does not yield sufficiently efficient algorithms in situations where configurations have to be included in a CI expansion which are more than triply excited with respect to a closed shell reference determinant.

Following the "unitary group" approach[18-26] some significant progress towards an efficient CI method for orthonormal basis sets containing multiply excited spin-adapted configurations has been made recently. In this approach the spins are coupled according to the YK scheme, the functions being labelled by means of "Gelfand tableaux".[18,19] This approach is based on the observation that the Hamiltonian operator is represented by second-quantized operators which can be identified with the generators of the Lie algebra of the unitary group U_n (n is the dimension of the spatial orbital basis). One can therefore express the matrix elements of the Hamiltonian by the matrix elements of these generators and their twofold products. Since the original formulation of Paldus,[20] which was suitable only for complete CI calculations, a number of advances have been made.

Segal *et al.*[22] developed a modification in which the weight factors C_{ij}^{ab} of the one-electron integrals in (1.1) are identified with the matrix elements of the generators in a canonically ordered CI basis which is labelled by an occupancy vector and a YK spin function. These weight factors C_{ij}^{ab} serve as a parameter list from which every weight factor C_{ijkl}^{ab} of the two electron integrals can be computed—generally by forming a scalar product of two $f_S^{N_o}$-tupels of C_{ij}^{ab} parameters. For up to eight open shells, Segal's parameter lists are of a size comparable to that of our approach, such that they can be stored in the central memory of a computer during matrix element evaluation. In comparison to our method more computational work has to be done for the determination of the weights of the two electron integrals from the parameters (cf. Sec. V). Thus, it seems that our approach might provide an even faster algorithm for CI matrix elements.

Ruttink[1] showed how Segal's C_{ij}^{ab} parameters can be determined from the YK representation matrices of a subset of all permutations $p \in S^{N_o}$. The considerable reduction of the size of the parameter lists achieved thereby allows the inclusion of configurations containing 10 and perhaps even 12 open shells, but at the expense of a further increase of computational work during matrix element generation (see also Sec. V).

Another modification of Paldus' version of the unitary group approach has been developed by Shavitt.[23-24] Brooks and Schaefer[25] presented an implementation of Shavitt's "graphical unitary group approach." This method involves an efficient algorithm (including up to n multiplications) for the creation of the weights C_{ij}^{ab} from a graphical representation of the CI basis and does not use a parameter list.

The CI method presented in this paper combines both the conceptual simplicity and clear separation of spin dependent and spatially dependent factors of the SAAP formalism and the simple book-keeping procedures of second quantization. Our second-quantized version of a SAAP formalism so far has been developed only for even numbered electron systems. For this case it establishes a promising alternative to the CI approaches discussed above which, however, are not limited to even electron systems. A computer program of our method, in the framework of a PPP–SCF–CI calculation but easily applicable to other electron Hamiltonians, is available upon request. This program requires as input the SCF matrix and the two-electron integrals and provides the CI matrix for any desired basis of single, double, triple, and quadruple singlet excitations with respect to a closed shell reference state.

II. SPIN SYMMETRY AND SECOND QUANTIZATION

In second quantization operators and wave functions are represented by linear combinations of algebraic products of creation and annihilation operators. The (anti-) commutation relations of these operators and their generalizations, e.g., in Wick's theorem,[63] are used in all algebraic manipulations. Although the spin coupling of these operators presents no serious problems,[63] to our knowledge no attempt has been made so far to develop a systematic theory of spin-coupled second-quantized operators.[64] It is the purpose of this section to develop the SAAP formalism in second quantization to provide the framework for the derivation of the matrix element formulas for a spin-free Hamiltonian.

A. Second quantization

The annihilation operator $a_{r_i\sigma_i}$ of an electronic spin orbital $|r_i\sigma_i\rangle$ is defined by its action on a Slater determinant

$$a_{r_i\sigma_i}||r_i r_2 \ldots r_k \sigma_i \sigma_2 \ldots \sigma_k\rangle\rangle = ||r_2 \ldots r_k \sigma_2 \ldots \sigma_k\rangle\rangle, \quad (2.1a)$$

$$a_{r_i\sigma_i}||r_1 r_2 \ldots r_k \sigma_1 \sigma_2 \ldots \sigma_k\rangle\rangle = 0$$

if

$$|r_i\sigma_i\rangle \notin \{|r_j\sigma_j\rangle \,|\, j=1,\ldots k\} \ . \quad (2.1b)$$

For $k=1$ we define

$$|0\rangle = a_{r\sigma}|r\sigma\rangle \quad (2.2a)$$

and call $|0\rangle$ the vacuum state, which we assume to be normalized:

$$\langle 0|0\rangle = 1 \ . \quad (2.2b)$$

The creation operators $a_{r\sigma}^{+}$ are the Hermitian conjugates of the annihilation operators. One has

$$a_{r\sigma}^{+}|0\rangle = |r\sigma\rangle \ , \quad (2.3)$$

$$a_{r_i\sigma_i}^{+}||r_1 \cdots r_k \sigma_1 \cdots \sigma_k\rangle\rangle = ||r_i r_1 \cdots r_k \sigma_i \sigma_1 \cdots \sigma_k\rangle\rangle$$

if

$$|r_i\sigma_i\rangle \notin \{|r_j\sigma_j\rangle \,|\, j=1,\ldots,k\} \ ,$$

$$a_{r_i\sigma_i}^{+}||r_1 \cdots r_k \sigma_1 \cdots \sigma_k\rangle\rangle = 0 \quad (2.4)$$

otherwise. From these definitions follow the anticommutation relations

$$[a_{r\sigma}, a_{r'\sigma'}]_+ = [a_{r\sigma}^{+}, a_{r'\sigma'}^{+}]_+ = 0 \ , \quad (2.5a)$$

$$[a_{r\sigma}^{+}, a_{r'\sigma'}]_+ = \delta_{r,r'}\delta_{\sigma,\sigma'} \ , \quad (2.5b)$$

where $[b,c]_+ = bc + cb$. The relations (2.5) account for the Fermion nature of the electrons and secure the antisymmetry property (1.10) of the wave functions constructed by means of Fermion operators. The Slater

determinants (1.25) are obtained by N-fold products of creation operators

$$||r_1\cdots r_N\sigma_1\cdots\sigma_N\rangle\rangle = a^+_{r_1\sigma_1}\cdots a^+_{r_N\sigma_N}|0\rangle \quad . \tag{2.6}$$

The one- and two-particle contributions to the Hamiltonian are in second quantization

$$\hat{Z} = \sum_{\substack{r_1r_2\\ \sigma_1\sigma_2}} \langle r_1\sigma_1|\hat{z}|r_2\sigma_2\rangle a^+_{r_1\sigma_1}a_{r_2\sigma_2} \quad , \tag{2.7a}$$

$$\hat{V} = \frac{1}{2}\sum_{\substack{r_1r_2r_3r_4\\ \sigma_1\sigma_2\sigma_3\sigma_4}} \langle r_1\sigma_1r_2\sigma_2|\hat{v}_{12}|r_3\sigma_3r_4\sigma_4\rangle a^+_{r_1\sigma_1}a^+_{r_2\sigma_2}a_{r_4\sigma_4}a_{r_3\sigma_3} \quad . \tag{2.7b}$$

The equalities hold only within the space spanned by the N-electron Slater determinantal basis.

B. Irreducible tensor operators[62]

Definition: Let S and M be integral or half integral, where $S \geq 0$, $-S \leq M \leq S$, and $S-M$ is an integer. The $2S+1$ operators ${}^{S,M}A$ are the *standard components* of a (*cogredient*) *irreducible tensor operator* (ITO) ${}^S\mathbf{A}$ of order S if ${}^{S,M}A$ obey the following commutation relations with the components of $\hat{\mathbf{S}}$

$$[\hat{S}_z, {}^{S,M}A] = M\,{}^{S,M}A \quad , \tag{2.8a}$$

$$[\hat{S}_\pm, {}^{S,M}A] = \sqrt{S(S+1)-M(M\pm1)}\,{}^{S,M\pm1}A \quad . \tag{2.8b}$$

Definition: The operators ${}^{S,M}A$ are the (*contra-*) *standard components* of a *contragredient* ITO ${}^S\mathbf{A}$ if

$$[{}^{S,M}A, \hat{S}_z] = M\,{}^{S,M}A \quad , \tag{2.9a}$$

$$[{}^{S,M}A, \hat{S}_\mp] = \sqrt{S(S+1)-M(M\pm1)}\,{}^{S,M\pm1}A \quad . \tag{2.9b}$$

These operators have the following properties:

(i) If ${}^S\mathbf{A}$ is an ITO with standard components ${}^{S,M}A$ and if ${}^S\mathbf{A}^+$ is the adjoint operator, then ${}^S\mathbf{A}^+$ is contragredient to ${}^S\mathbf{A}$.

(ii) From a contragredient ITO ${}^S\mathbf{A}$ with standard components ${}^{S,M}A$ one obtains by means of the transformation

$${}^S\mathbf{U}: {}^S\mathbf{A} \rightarrow {}^S\mathbf{B} = {}^S\mathbf{U}\,{}^S\mathbf{A} \tag{2.10a}$$

defined by

$${}^{S,\bar{M}}B = \sum_{M=-S}^{S} {}^SU_{\bar{M},M}\,{}^{S,M}A \tag{2.10b}$$

$${}^SU_{\bar{M},M} = (-1)^{S+\bar{M}}\delta_{\bar{M},-M} \tag{2.10c}$$

a (cogredient) ITO ${}^S\mathbf{B}$ with standard components ${}^{S,\bar{M}}B$.

(iii) The standard components of an ITO are uniquely determined up to a sign.

Definition: Let ${}^S\mathbf{A}$ be an ITO. The corresponding cogredient ITO ${}^S\mathbf{U}\,{}^S\mathbf{A}^+$ is called the *conjugate* of ${}^S\mathbf{A}$.

(iv) For integral S this relationship of conjugation is reciprocal. For half-integral S it is reciprocal to within a factor -1.

Definition: Let the operators ${}^{S'}\mathbf{A}$ and ${}^{S''}\mathbf{B}$ be two ITO's with standard components ${}^{S',M'}A$ and ${}^{S'',M''}B$. The *irreducible product* (IP) ${}^S[{}^{S'}\mathbf{A}\otimes{}^{S''}\mathbf{B}]$ of degree S of ${}^{S'}\mathbf{A}$ and ${}^{S''}\mathbf{B}$ is given by

$${}^{S,M}[{}^{S'}\mathbf{A}\otimes{}^{S''}\mathbf{B}] = \sum_{M',M''} (SM|S'M'S''M'')\,{}^{S',M'}A\otimes{}^{S'',M''}B \quad . \tag{2.11}$$

Here $(SM|S'M'S''M'')$ are the Wigner coefficients[62] and ${}^{S,M}[{}^{S'}\mathbf{A}\otimes{}^{S''}\mathbf{B}]$ are the components of the IP. The product $\otimes$ of the components in (2.11) denotes the usual tensor product of elements ${}^{S',M'}A$ and ${}^{S'',M''}B$ of a linear space. The product might, however, be any other algebraic product defined in the tensorial set of the components. In any case the following statement is true.

(v) The IP (2.11) is an ITO not necessarily different from zero. If the product does not vanish, we have $S'+S'' \geq S \geq |S'-S''|$ and $S+S'+S''$ is an integer.

(vi) If in particular the product $\otimes$ of the components is a tensor product: The IP is different from zero and the transformation $(SM|S'M'S''M'')$ which reduces the tensorial set of products ${}^{S',M'}A\otimes{}^{S'',M''}B$ is orthogonal. This statement does not change if $\otimes$ is considered as a symmetrized tensor product, i.e., as an algebraic product of commuting operators.

Definition: We call ITO's of order 0 *singlet operators*, those of order 1 *triplet operators* etc.

C. Irreducible creation operators create spin eigenfunctions

Suppose the basis $\{|i\rangle, i=1,\ldots\}$ of a Hilbert space $\mathbf{H}$ is created by the application of operators A_i^+ to a normalized reference state $|0\rangle$:

$$A_i^+|0\rangle = |i\rangle \quad i=1,2\ldots \tag{2.12a}$$

$$\langle 0|0\rangle = 1 \quad . \tag{2.12b}$$

Let furthermore $\{\hat{O}_\alpha | \alpha=1,\ldots,m\}$ be a set of m operators on $\mathbf{H}$ which annihilate the reference state $|0\rangle$:

$$\hat{O}_\alpha|0\rangle = 0 \quad \alpha=1,\ldots,m \quad . \tag{2.13}$$

Then the following statement holds: If one of the operators $\hat{O}_\alpha$ has commutation relations with the creation operators A_i^+ of the form

$$[\hat{O}_\alpha, A_i^+] = o_\alpha(i)A_i^+ + \sum_{\beta\in M} c_\beta A_i^+\hat{O}_\beta \quad , \tag{2.14}$$

where the index set $M \subset [1,m]$ may also be empty and where the $o_\alpha(i)$ and the c_β are real numbers, then $\hat{O}_\alpha$ is diagonal in the $|i\rangle$ basis

$$\hat{O}_\alpha|i\rangle = o_\alpha(i)|i\rangle \quad . \tag{2.15}$$

Identification of such $\hat{O}_\alpha$ with either of the total spin operators $\hat{\mathbf{S}}^2$ and $\hat{S}_z$ [for which commutation relations of the form (2.14) can be derived from (2.8)] yields:

Theorem: If the creation operators A_i^+ are standard components of ITO's and if the reference state $|0\rangle$ is a singlet state, i.e.,

$$\hat{S}_z|0\rangle = \hat{S}_\pm|0\rangle = 0 \quad , \tag{2.16}$$

then the A_i^+ create eigenstates of the total spin operators $\hat{\mathbf{S}}^2$ and $\hat{S}_z$.

These irreducible creation operators A_i^+ may be the operators which create an N-electron SAAP-basis (1.26) from the vacuum state. They may also be identified with the creation operators $a_{r\sigma}^+$ of the one electron space since these are also components of ITO's.

D. Irreducible Fermion operators

Theorem: The two operators $a_{r\alpha}^+$ and $a_{r\beta}^+$ defined by (2.3) and (2.4) are the standard components of an ITO $\mathbf{a}_r^+$ of order 1/2.[65]

Obviously the two component operator $\mathbf{a}_r^+$ is the second-quantized analogue to a spatial orbital $|\phi_r\rangle$. Furthermore we immediately see that the adjoint operators $(a_{r\alpha}, a_{r\beta})$ are contrastandard to $(a_{r\alpha}^+, a_{r\beta}^+)$. According to (2.10) we obtain by means of the transformation

$$\mathbf{U}: \mathbf{a}_r - \mathbf{b}_r = \mathbf{U}\mathbf{a}_r \tag{2.17a}$$

given by

$$\begin{pmatrix} b_{r\alpha} \\ b_{r\beta} \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a_{r\alpha} \\ a_{r\beta} \end{pmatrix} \tag{2.17b}$$

the conjugate $\mathbf{b}_r$ of $\mathbf{a}_r^+$, which is again an (cogredient) ITO. The conjugation is unique up to a sign.

From these ITO's $\mathbf{a}_r^+$ and $\mathbf{U}\mathbf{a}_r$ we can construct now a variety of IP's which *orthogonally* reduce the corresponding *tensor products* $\otimes$ of the standard components. Having chosen an appropriate coupling scheme the standard components of such q-fold irreducible tensor products assume the form (cf. Appendix I E)

$$\begin{aligned} &{}^{S,M}_{k}[\mathbf{c}_{r_1} \otimes \cdots \otimes \mathbf{c}_{r_q}] \\ &= \sum_{\sigma_1 \cdots \sigma_q} {}^{S,M}_{k}T_{\sigma_1 \ldots \sigma_q} c_{r_1\sigma_1} \otimes \cdots \otimes c_{r_q\sigma_q} \ , \end{aligned} \tag{2.18}$$

where $\mathbf{c}_r \in \{\mathbf{a}_r^+, \mathbf{U}\mathbf{a}_r\}$, $\sigma \in \{\alpha, \beta\}$, and where the orthogonality relation for the reducing transformation $\mathbf{T}$ is given by (A1.7).

Unfortunately, the construction (2.18) of ITO's is not directly applicable to operators of second quantization. As one can see from the anticommutation rules (2.5) the products of these operators are not simple tensor products "$\otimes$", but, with the exception of the product between $c_{r\sigma}$ and its adjoint $c_{r\sigma}^+$, are skew symmetric tensor products "$\wedge$" (see for example Ref. 66)

$$c_{r_1\sigma_1} \cdots c_{r_q\sigma_q} = c_{r_1\sigma_1} \wedge \cdots \wedge c_{r_q\sigma_q}$$

if

$$c_{r_i\sigma_i} \neq c_{r_j\sigma_j}^+, i, j = 1, \ldots, q \ . \tag{2.19}$$

The skew symmetric tensor product "$\wedge$" is defined by the application of an appropriate antisymmetrizer $\bar{A}$ to the factors of the tensor product

$$c_{r_1\sigma_1} \wedge \cdots \wedge c_{r_q\sigma_q} = \sqrt{q!}\, \bar{A}\, (c_{r_1\sigma_1} \otimes \cdots \otimes c_{r_q\sigma_q}) \ . \tag{2.20}$$

"Appropriate" is to imply, that $\bar{A}$ antisymmetrizes the factors in a tensor product of Fermion operators $c_{r\sigma}$. This is in contrast to the action of the antisymmetrizer $\hat{A}$ defined by (1.24) which applies to the arguments of a function. To establish the relationship between a permutation operator $\bar{P}$ on the Fermion operators and the permutation operator $\hat{P}$ on the coordinates we consider the action of $\bar{P}$ on a q-fold tensor product of creation operators $a_{r\sigma}^+$. In this case $\bar{P}$ can be identified with a permutation operator on spin orbitals and one has (cf. Ref. 17 and Appendix I E)

$$\bar{P}\, a_{r_1\sigma_1}^+ \otimes \cdots \otimes a_{r_q\sigma_q}^+ |0\rangle = \hat{P}^{-1}\, a_{r_1\sigma_1}^+ \otimes \cdots \otimes a_{r_q\sigma_q}^+ |0\rangle \ , \tag{2.21}$$

i.e., $\bar{P}$ corresponds to $\hat{P}^{-1}$. Since the permutation operators $\bar{P}$ commute with the spin operators $\hat{\mathbf{S}}^2$ and $\hat{S}_z$, antisymmetrization of the irreducible tensor product defined by (2.18) yields again an ITO:

$${}^{S,M}_{k}[\mathbf{c}_{r_1} \wedge \cdots \wedge \mathbf{c}_{r_q}] = \sqrt{q!}\, \bar{A}\ {}^{S,M}_{k}[\mathbf{c}_{r_1} \otimes \cdots \otimes \mathbf{c}_{r_q}] \ . \tag{2.22}$$

Definition: We call the ITO's ${}^{S}_{k}[\mathbf{c}_{r_1} \wedge \cdots \wedge \mathbf{c}_{r_q}]$ defined by (2.22) *antisymmetrized irreducible products or* AIP's.

The AIP's reduce the tensorial set of the corresponding skew symmetric tensor products (2.20). *Their standard components are operators of second quantization if the condition in* (2.19) *holds for this tensorial set.* The reducing transformation is not necessarily orthogonal since some of the terms in the sum (2.18) may vanish upon antisymmetrization. Thus, the standard components of the AIP's (2.22) are not necessarily normalized.

Definition: Let $\mathbf{C} = (\mathbf{c}_{r_1}, \ldots, \mathbf{c}_{r_q})$ be an ordered set of irreducible Fermion operators $\mathbf{c}_r \in \{\mathbf{a}_r^+, \mathbf{U}\mathbf{a}_r\}$. $\mathbf{C}$ defines a set $\mathbf{C}$ of ordered algebraic products of the components $c_{r\sigma}$

$$\mathbf{C} = \{c_{r_1\sigma_1} \cdots c_{r_q\sigma_q} \,|\, \sigma_i = \alpha, \beta;\ i = 1, \ldots, q\}. \tag{2.23a}$$

If an operator $\mathbf{c}_{r_i}$ occurs more than once in $\mathbf{C}$ then some of the elements of $\mathbf{C}$ may vanish because of the anticommutation relation (2.5a). Let therefore $\mathbf{C}' \subset \mathbf{C}$ be the subset of the nonvanishing operator products ($|\mathbf{C}'| \leq |\mathbf{C}| = 2^q$) and let $\mathbf{C}''$ be a set of standard components ${}^{S,M}_{k}[\mathbf{c}_{r_1} \cdots \mathbf{c}_{r_q}]$ of ITO's ${}^{S}_{k}[\mathbf{c}_{r_1} \cdots \mathbf{c}_{r_q}]$ obtained from $\mathbf{C}'$ by an *orthogonal* reducing transformation

$$\mathbf{D}: \mathbf{C}' - \mathbf{C}''$$

which obeys

$$\begin{aligned} &{}^{S,M}_{k}[\mathbf{c}_{r_1} \cdots \mathbf{c}_{r_q}] \\ &= \sum_{\sigma_1 \cdots \sigma_q} {}^{S,M}_{k}D_{\sigma_1 \cdots \sigma_q}\, c_{r_1\sigma_1} \cdots c_{r_q\sigma_q} \ , \end{aligned} \tag{2.23b}$$

where

$${}^{S,M}_{k}D_{\sigma_1 \cdots \sigma_q} = 0 \quad \text{if} \quad c_{r_1\sigma_1} \cdots c_{r_q\sigma_q} = 0 \tag{2.23c}$$

and

$$\begin{aligned} &\sum_{\sigma_1 \cdots \sigma_q} {}^{S,M}_{k}D_{\sigma_1 \cdots \sigma_q}\ {}^{S',M'}_{k'}D_{\sigma_1 \cdots \sigma_q} \\ &= \delta_{S,S'}\, \delta_{M,M'}\, \delta_{k,k'} \ . \end{aligned} \tag{2.23d}$$

We call the standard components ${}^{S,M}_{k}[\mathbf{c}_{r_1} \cdots \mathbf{c}_{r_q}]$ *normalized spin-coupled operators of second quantization.* Furthermore we call all linear combinations of these operators corresponding to a certain pair (S, M) *spin-coupled operators of second quantization.*

The standard components (2.22) of those AIP's which obey the condition

$$\mathbf{c}_{r_i} \neq \pm \mathbf{U}\mathbf{c}^+_{r_j} \quad i,j=1,\ldots,q \tag{2.24a}$$

become normalized spin-coupled operators of second quantization when an appropriate normalization constant K has been determined

$$^{S,M}_{k}[\mathbf{c}_{r_1}\cdots\mathbf{c}_{r_q}] = K\ ^{S,M}_{k}[\mathbf{c}_{r_1}\wedge\cdots\wedge\mathbf{c}_{r_q}] \tag{2.24b}$$

$$K = K(r_1,\ldots,r_q). \tag{2.24c}$$

The determination of K, or equivalently the determination of the reducing transformation $\mathbf{D}$ (2.23) from the reducing transformation $\mathbf{T}$ (2.18), is particularly simple if all factors in the AIP are different. In this case

$$K=1 \quad \text{if} \quad \mathbf{c}_{r_i} \neq \mathbf{c}_{r_j} \quad i,j=1,\ldots,q \tag{2.25}$$

i.e., $\mathbf{D}$ and $\mathbf{T}$ are identical. In all other cases the determination of K is nontrivial.

As exhibited by the normalization factor in (1.26) a related problem occurs in first quantization in the construction of an orthonormal SAAP basis. For the SAAP's one can determine the orthogonal transformation reducing the Slater determinant basis to the SAAP basis by means of the representation theory of the permutation group (cf. Ref. 15 or Ref. 16). For this purpose one separates and then separately permutes space and spin parts of the wave function [see (1.14)–(1.21), (1.26), and (1.27)]. In the following we will show how one can separate quite analogously spin and space parts of the Fermion operators and how the representation theory of the permutation group enters second quantization.

E. Separation of spin and space parts in second quantization

Let $\hat{\alpha}$ and $\hat{\beta}$ be the two linear mappings which map the irreducible tensor operator $\mathbf{a}^+_\tau$ or its conjugate operator $\mathbf{U}\mathbf{a}_\tau$ on their standard components:

$$\hat{\alpha}(\mathbf{a}^+_\tau) = a^+_{\tau\alpha} \quad \hat{\beta}(\mathbf{a}^+_\tau) = a^+_{\tau\beta} \tag{2.26a}$$

or

$$\hat{\alpha}(\mathbf{U}\mathbf{a}_\tau) = -a_{\tau\beta} \quad \hat{\beta}(\mathbf{U}\mathbf{a}_\tau) = a_{\tau\alpha} \ . \tag{2.26b}$$

These mappings can be conceived as the ordinary one particle spin functions α and β. We will therefore identify $\hat{\alpha} \equiv \alpha$ and $\hat{\beta} \equiv \beta$.

To demonstrate the relationship between $\hat{\sigma}$ and σ we note that the creation operators $\{a^+_{r\sigma} | r=1,2,\ldots;\ \sigma=\alpha,\beta\}$ span a unitary space $\mathbf{A}^+$. Its scalar product is given by

$$(a^+_{r\sigma}|a^+_{r'\sigma'}) = \langle 0|a_{r\sigma}\, a^+_{r'\sigma'}|0\rangle = \delta_{r,r'}\,\delta_{\sigma,\sigma'} \ .$$

Likewise, the two component irreducible Fermion creation operators $\{\mathbf{a}^+_\tau = (a^+_{r\alpha}, a^+_{r\beta}) | r=1,2,\ldots\}$ span a unitary space $\hat{\mathbf{A}}^+$. Then the linear mappings $\hat{\sigma}: \mathbf{a}^+_\tau \in \hat{\mathbf{A}}^+ \rightarrow \hat{\sigma}(\mathbf{a}^+_\tau) \in \mathbf{A}^+$ defined by (2.26a) span a two dimensional space $\hat{\mathbf{E}}^\sigma$. Its linear structure is induced by the linear structure of $\mathbf{A}^+$

$$(\lambda\hat{\sigma} + \lambda'\hat{\sigma}')(\mathbf{a}^+_\tau) = \lambda\hat{\sigma}(\mathbf{a}^+_\tau) + \lambda'\hat{\sigma}'(\mathbf{a}^+_\tau)$$

and its scalar product is induced by the scalar product of $\mathbf{A}^+$

$$(\hat{\sigma}|\hat{\sigma}') = (\hat{\sigma}(\mathbf{a}^+_\tau)|\hat{\sigma}'(\mathbf{a}^+_\tau)) = \delta_{\sigma,\sigma'} \quad \tau=1,2,\ldots$$

An operator $\hat{O}$, the matrix representation of which $O_{r\sigma,r'\sigma'} = (a^+_{r\sigma}|\hat{O}a^+_{r'\sigma'})$ assumes in $\mathbf{A}^+$ the form $O_{r\sigma,r'\sigma'} = \delta_{r,r'}\, O_{\sigma,\sigma'}$, in $\hat{\mathbf{E}}^\sigma$ has the matrix representation $O_{\sigma,\sigma'}$. Since the spin operators are diagonal in $\mathbf{A}^+$ they are so in $\hat{\mathbf{E}}^\sigma$ and assume the same form as in the usual spin 1/2 space $\mathbf{E}^\sigma$.

The proof for the conjugate spin operator $\mathbf{U}\mathbf{a}_\tau$ is identical if one conceives its components $(-a_{r\beta}, a_{r\alpha})$ as hole creation operators rather than as electron annihilation operators, i.e., if one defines the scalar product in the "hole space" $\mathbf{A}$[spanned by $\{a_{r\sigma} | r=1,2,\ldots;\sigma=\alpha,\beta\}$ by

$$(a_{r\sigma}|a_{r'\sigma'}) = \langle 0|a_{r\beta}a_{r\alpha}a^+_{r\sigma}a_{r'\sigma'}a^+_{r\alpha}a^+_{r\beta}|0\rangle$$

[This definition obviously matches the definition of the scalar product for the hole creation operators of the particle–hole formalism of second quantization (see Sec. III) so that the above separation of spin and space parts is valid for all creation operators in this formalism. Thus, it can be used for the construction of spin-coupled excitation operators.]

The usual q-particle spin functions (A1.6) are linear combinations of q-fold tensor products $\sigma_1 \otimes \cdots \otimes \sigma_q$. We can conceive these products as q-linear mappings which attach to the q-fold tensor product of operators $\mathbf{a}^+_\tau$ and $\mathbf{U}\mathbf{a}_\tau$ the components of the corresponding irreducible tensor product (2.18), i.e.,

$$\Theta^q_{S,M,k}(\mathbf{c}_{r_1}\otimes\cdots\otimes\mathbf{c}_{r_q}) = {}^{S,M}_{k}[\mathbf{c}_{r_1}\otimes\cdots\otimes\mathbf{c}_{r_q}] \ . \tag{2.27a}$$

The action of $\Theta^q_{S,M,k}$ is defined through

$$\sigma_1\otimes\cdots\otimes\sigma_q(\mathbf{c}_{r_1}\otimes\cdots\otimes\mathbf{c}_{r_q}) = \sigma_1(\mathbf{c}_{r_1})\otimes\cdots\otimes\sigma_q(\mathbf{c}_{r_q}) \ . \tag{2.27b}$$

The $\sigma_i(\mathbf{c}_{r_i})$ are given by (2.26). Assuming that condition (2.24a) holds for the factors $\mathbf{c}_{r_i}$ of the irreducible tensor product (2.27a), we can consider the $\sigma_i(\mathbf{c}_{r_i})$ as particle or hole *creation* operators. Furthermore, the AIP obtained by antisymmetrization of (2.27a), i.e.,

$$^{S,M}_{k}[\mathbf{c}_{r_1}\wedge\cdots\wedge\mathbf{c}_{r_q}] = \sqrt{q!}\,\bar{A}\,\Theta^q_{S,M,k}(\mathbf{c}_{r_1}\otimes\cdots\otimes\mathbf{c}_{r_q}) \ , \tag{2.28}$$

is a spin-coupled operator of second quantization which assumes a representation with spin and space parts separated. This separation admits the introduction of the representation theory of the permutation group into the calculus of second quantization (see below).

The spin mapping (2.26) offers for yet another subclass of spin-coupled operators of second quantization a possible construction by means of q-particle spin functions $\Theta^q_{S,M,k}$. In fact, the ITO's $^{S}_{k}[\mathbf{c}_{r_1}\cdots\mathbf{c}_{r_q}]$ defined by (2.23), for which the elements of the q-tupel $\mathbf{C}$ are all different

$$\mathbf{c}_{r_i} \neq \mathbf{c}_{r_j} \quad i,j=1,\ldots,q \tag{2.29a}$$

are irreducible products reducing the algebraic products (2.23a). This follows from the identity of $\mathbf{C}$ and $\mathbf{C}'$ which in turn implies the identity of the reducing transformations $\mathbf{D}$ (2.23) and $\mathbf{T}$ (2.18) [cf. (2.25)]. As a result one can consider a q-particle spin function $\Theta^q_{S,M,k}$ as a mapping of the q-tupel $\mathbf{C}$ into the set $\mathbf{C}''$:

$$\Theta^q_{S,M,k}(\mathbf{c}_{r_1},\ldots,\mathbf{c}_{r_q}) = {}^{S,M}_{k}[\mathbf{c}_{r_1}\cdots\mathbf{c}_{r_q}] \tag{2.29b}$$

where the action of a q-fold tensor product $\sigma_1 \otimes \cdots \otimes \sigma_q$ on $\mathbf{C}$ is

$$\sigma_1 \otimes \cdots \otimes \sigma_q(\mathbf{c}_{r_1}, \ldots, \mathbf{c}_{r_q}) = \sigma_1(\mathbf{c}_{r_1}) \cdots \sigma_q(\mathbf{c}_{r_q}) \quad . \tag{2.30}$$

$\sigma(\mathbf{c}_r)$ is defined by (2.26) and the product on the rhs of (2.30) is the algebraic product of Fermion operators. The spin-coupled operators (2.29) are obviously normalized.

F. Transformation properties of AIP's upon permutations

Theorem: Let $\overline{P}^r$ denote the permutation operator which causes a permutation p^{-1} of the factors $\mathbf{c}_r$ in the AIP (2.28)

$$\overline{P}^r\, {}^{S,M}_{k}[\mathbf{c}_{r_1} \wedge \cdots \wedge \mathbf{c}_{r_q}] = {}^{S,M}_{k}[\mathbf{c}_{r_{p^{-1}(1)}} \wedge \cdots \wedge \mathbf{c}_{r_{p^{-1}(q)}}] \quad . \tag{2.31}$$

Then

$$\overline{P}^r\, {}^{S,M}_{k}[\mathbf{c}_{r_1} \wedge \cdots \wedge \mathbf{c}_{r_q}] = \sum_l U^{Sq}_{lk}(p)\, {}^{S,M}_{l}[\mathbf{c}_{r_1} \wedge \cdots \wedge \mathbf{c}_{r_q}] \tag{2.32}$$

i.e., the AIP's transform upon permutations according to the irreducible representation (1.15) of the symmetric group S^q.

For a proof we note

$$\begin{aligned}
\overline{P}^r\, {}^{S,M}_{k}[\mathbf{c}_{r_1} \wedge \cdots \wedge \mathbf{c}_{r_q}] &= \sqrt{q!}\, \overline{A}\, \Theta^q_{S,M,k}[\overline{P}^r(\mathbf{c}_{r_1} \otimes \cdots \otimes \mathbf{c}_{r_q})] \\
&= \frac{1}{\sqrt{q!}} \sum_{p' \in S^q} \epsilon(p') \overline{P}'^{\sigma}\, \Theta^q_{S,M,k}[\overline{P}'^{r}\, \overline{P}^r(\mathbf{c}_{r_1} \otimes \cdots \otimes \mathbf{c}_{r_q})] \\
&= \frac{1}{\sqrt{q!}} \sum_{p'' \in S^q} \epsilon(p'')\epsilon(p) \overline{P}''^{\sigma}\, \overline{P}^{\sigma^{-1}}\, \Theta^q_{S,M,k}[\overline{P}''^{r}(\mathbf{c}_{r_1} \otimes \cdots \otimes \mathbf{c}_{r_q})] \\
&= \epsilon(p)\sqrt{q!}\, \overline{A} \sum_l V^{Sq}_{lk}(p) \Theta^q_{S,M,l}(\mathbf{c}_{r_1} \otimes \cdots \otimes \mathbf{c}_{r_q}) \quad .
\end{aligned}$$

Remark: We have dropped above the differentiation between an AIP and its components. We will continue to do so whenever there is no danger of confusion.

G. The scalar product of AIP's

Let B^+ and B'^+ be two q-fold products of Fermion creation operators

$$B^+ = a^+_{r_1\sigma_1} \cdots a^+_{r_q\sigma_q} \quad , \tag{2.33a}$$

$$B'^+ = a^+_{r_1\sigma_1} \cdots a^+_{r_q\sigma_q} \quad . \tag{2.33b}$$

The scalar product is defined by

$$(B^+ | B'^+) = \langle 0 | B\, B'^+ | 0 \rangle \quad . \tag{2.34a}$$

Application of Wick's theorem[63] yields

$$\begin{aligned}
(B^+ | B'^+) = \sum_{p \in S^q} \epsilon(p) \delta(r_1 \cdots r_q, r'_{p(1)} \cdots r'_{p(q)}) \\
\times \delta(\sigma_1 \cdots \sigma_q, \sigma'_{p(1)} \cdots \sigma'_{p(q)})
\end{aligned} \tag{2.34b}$$

where

$$\delta(x_1 \cdots x_q, y_1 \cdots y_q) = \delta_{x_1,y_1} \cdots \delta_{x_q,y_q} \quad . \tag{2.35}$$

Let

$${}^{S,M}_{k}B^+ = {}^{S,M}_{k}[\mathbf{a}^+_{r_1} \wedge \cdots \wedge \mathbf{a}^+_{r_q}] \quad , \tag{2.36a}$$

$${}^{S',M'}_{k'}B'^+ = {}^{S',M'}_{k'}[\mathbf{a}^+_{r'_1} \wedge \cdots \wedge \mathbf{a}^+_{r'_q}] \tag{2.36b}$$

be two AIP's of creation operators. Their scalar product is

$$({}^{S,M}_{k}B^+ | {}^{S',M'}_{k'}B'^+) = \delta_{S,S'}\, \delta_{M,M'} \sum_{p \in S^q} \epsilon(p) V^{Sq}_{kk'}(p) \delta(r_1 \cdots r_q, r'_{p(1)} \cdots r'_{p(q)}) \tag{2.37}$$

To show this we note

$$\begin{aligned}
({}^{S,M}_{k}B^+ | {}^{S',M'}_{k'}B'^+) &= \sum_{\substack{\sigma_1 \cdots \sigma_q \\ \sigma'_1 \cdots \sigma'_q}} {}^{S,M}_{k}T_{\sigma_1 \cdots \sigma_q}\, {}^{S',M'}_{k'}T_{\sigma'_1 \cdots \sigma'_q} (B^+ | B'^+) \\
&= \sum_{p \in S^q} \epsilon(p) \delta(r_1 \cdots r_q, r'_{p(1)} \cdots r'_{p(q)}) \sum_{\substack{\sigma_1 \cdots \sigma_q \\ \sigma'_1 \cdots \sigma'_q}} {}^{S,M}_{k}T_{\sigma_1 \cdots \sigma_q}\, {}^{S',M'}_{k'}T_{\sigma'_1 \cdots \sigma'_q}\, \delta(\sigma_1 \cdots \sigma_q, \sigma'_{p(1)} \cdots \sigma'_{p(q)}) \\
&= \sum_{p \in S^q} \epsilon(p) \delta(r_1 \cdots r_q, r'_{p(1)} \cdots r'_{p(q)}) \sum_{\sigma_1 \cdots \sigma_q} {}^{S,M}_{k}T_{\sigma_1 \cdots \sigma_q}\, {}^{S',M'}_{k'}T_{\sigma_{p^{-1}(1)} \cdots \sigma_{p^{-1}(q)}} \quad .
\end{aligned}$$

The properties (A 1.11) and (A 1.7) of the reducing transformation $\mathbf{T}$ show then assertion (2.37) to be correct.

Equation (2.34b) is also valid for q-fold products of particle and hole creation operators if one defines the scalar product (2.34a) with respect to a "Fermi-vacuum" (see next section) rather than with respect to the true vacuum. We have used for the proof of (2.37) only (2.34b) and the properties of the reducing transformation $\mathbf{T}$. Therefore (2.37) is also valid for AIP's (2.28) of particle–hole creation operators.

III. SAAP CREATION OPERATORS

In this section we want to construct an orthonormal SAAP basis for the $2N_h$ electron space. For this purpose we introduce the particle–hole ("*ph*") formalism of second quantization which allows to focus on the few electrons excited from a closed shell ("CS") reference state and to suppress any explicit consideration of the many remaining electrons.

A. Particles and holes

The (ground) reference state $|\,|0\rangle\rangle$ of the $2N_h$ electron system is described by a single Slater determinant built

up from N_h doubly occupied orbitals $|\phi_r\rangle$

$$||0\rangle\rangle = a^+_{r_1\alpha}\, a^+_{r_1\beta} \cdots a^+_{r_{N_h}\alpha}\, a^+_{r_{N_h}\beta}|0\rangle \tag{3.1}$$

and is called "Fermi vacuum." In the following the orbitals occupied in $||0\rangle\rangle$ will be denoted by the letters g, i, j, k

$$1 \le g, i, j, k \le N_h \ , \tag{3.2a}$$

the unoccupied orbitals by l, m, n, o

$$N_h + 1 \le l, m, n, o \le N_h + N_p \ . \tag{3.2b}$$

A single excitation involves the creation of a hole in an occupied orbital followed by the creation of a particle in an unoccupied orbital. The hole creation operators are

$$h^+_i = a_{i\alpha} \qquad \bar{h}^+_i = a_{i\beta} \tag{3.3}$$

and the particle creation operators are

$$p^+_i = a^+_{i\alpha} \qquad \bar{p}^+_i = a^+_{i\beta} \ . \tag{3.4}$$

These operators and their adjoint annihilation operators obey the anticommutation rules (2.5). In particular, the particle operators anticommute with the hole operators, and the hole as well as the particle annihilation operators annihilate the Fermi vacuum

$$h_i||0\rangle\rangle = \bar{h}_i||0\rangle\rangle = p_i||0\rangle\rangle = \bar{p}_i||0\rangle\rangle = 0 \ . \tag{3.5}$$

Operators of the form

$$\tilde{A}^+_\nu = \prod_{\kappa=1}^{\nu} \tilde{p}^+_\kappa \tilde{h}^+_\kappa \ , \qquad \nu = 1, \ldots, 2N_h \ , \tag{3.6}$$

with

$$\tilde{p}^+_\kappa \in \{p^+_i, \bar{p}^+_i\} \quad \text{and} \quad \tilde{h}^+_\kappa \in \{h^+_i, \bar{h}^+_i\} \ , \tag{3.7}$$

applied to the Fermi vacuum create a ν-fold excited spin orbital configuration. The CI basis (1.25) is composed of the set of all ν-fold excitation operators (3.6). The dimension of the space $\tilde{\mathbf{A}}^{(\nu)}$ of the ν-fold excitation operators (3.6) is

$$\dim \tilde{\mathbf{A}}^{(\nu)} = \binom{2N_h}{\nu}\binom{2N_p}{\nu} \ . \tag{3.8}$$

The dimension of the complete $2N_h$ electron space is (see also Ref. 17)

$$\dim \left(\bigoplus_{\nu=0}^{2N_h} \tilde{\mathbf{A}}^{(\nu)} \right) = \binom{2(N_h+N_p)}{2N_h} \ . \tag{3.9}$$

B. The SAAP creation operators

In order to reduce the dimension of the matrix eigenvalue problem (1.5) we have to construct spin-coupled excitation operators ${}^{S,M}_{k}A^+_\nu$ from the $\tilde{A}^+_\nu$ which, when applied to the Fermi vacuum, yield an orthonormal SAAP basis. For the construction of these SAAP creation operators an orthogonal reducing transformation is applied to the tensorial set of excitation operators $\tilde{A}^+_\nu$.

The ν-fold excitation operators $\tilde{A}^+_\nu$ are ν-fold geminal products of operators $\tilde{p}^+_\kappa$ and $\tilde{h}^+_\kappa$. The latter are standard components of the irreducible tensor operators

$$\mathbf{p}^+_i = (p^+_i, \bar{p}^+_i) \quad \text{and} \quad \mathbf{Uh}^+_i = (-\bar{h}^+_i, h^+_i) \tag{3.10}$$

of order $\frac{1}{2}$. Hence, the SAAP *creation operators* ${}^{S,M}_{k}A^+_\nu$ are obtained as normalized spin-coupled operators according to (cf. Sec. IIC and Sec. IID)

$${}^{S,M}_{k}A^+_\nu(\mathbf{L},\mathbf{I}) = {}^{S,M}_{k}[\mathbf{p}^+_{i_1}\mathbf{Uh}^+_{i_1} \cdots \mathbf{p}^+_{i_\nu}\mathbf{Uh}^+_{i_\nu}] \ . \tag{3.11}$$

$(\mathbf{L},\mathbf{I})$ denotes the orbital configuration

$$(\mathbf{L},\mathbf{I}) = (l_1, i_1, \ldots, l_\nu, i_\nu) \tag{3.12}$$

in which none of the orbital indices occurs more than twice. Since condition (2.24a) holds for the SAAP creation operators (3.11) the latter according to (2.24b) can be represented as AIP's of irreducible particle and hole creation operators (3.10)

$${}^{S,M}_{k}B^+_\nu(\mathbf{L},\mathbf{I}) = \sqrt{(2\nu)!}\ \bar{A}\, \Theta^{2\nu}_{S,M,k}\, (\mathbf{p}^+_{i_1} \otimes \mathbf{Uh}^+_{i_1} \otimes \cdots \otimes \mathbf{p}^+_{i_\nu} \otimes \mathbf{Uh}^+_{i_\nu}) \ . \tag{3.13}$$

by means of an appropriate normalization constant. The excitation operators, orbital configurations, and spin coupling schemes occurring in this section are illustrated in Fig. 1. The reader is advised to repeatedly consult this figure in the following. We will show now that in the *Serber coupling scheme* the relation between the SAAP creators (3.11) and the AIP's (3.13) is simply

$${}^{S,M}_{k}A^+_\nu(\mathbf{L},\mathbf{I}) = 2^{|\Delta M^{ph}_{CS}|/2}\ {}^{S,M}_{k}B^+_\nu(\mathbf{L},\mathbf{I}) \tag{3.14a}$$

where the numbers ΔM^{ph}_{CS}, the orbital configurations $(\mathbf{L},\mathbf{I})$ and the Serber functions $\Theta^{2\nu}_{S,M,k}$ are defined in the following way:

(i) M_h denotes the number of hole closed shells (CS) created by the SAAP creator (3.11), i.e., $2M_h$ is the number of orbital indices i_κ occurring twice in $(\mathbf{L},\mathbf{I})$. Analogously the number of particle CS created by (3.11) is denoted by M_p. Then

$$\Delta M^{ph}_{CS} = M_p - M_h \ . \tag{3.14b}$$

(ii) In the orbital configuration $(\mathbf{L},\mathbf{I})$ the particle indices l_κ and the hole indices i_κ are ordered in an alternating sequence (*"phph"*) according to the following prescription: The first $2M_p$ particle indices and the first $2M_h$ hole indices denote the closed shells of the excitation with orbital indices ascending from left to right. The remaining particle and hole orbital indices of the singly occupied shells created by (3.11) also increase from left to right. This is summarized for the holes by the relations

$$\begin{aligned} &1 \le \kappa < 2M_h \Rightarrow \begin{cases} i_\kappa = i_{\kappa+1} & \text{if} \quad \kappa \text{ odd} \\ i_\kappa < i_{\kappa+1} & \text{if} \quad \kappa \text{ even} \end{cases} \\ &2M_h + 1 \le \lambda < 2\nu \Rightarrow i_\lambda < i_{\lambda+1} \\ &1 \le \kappa \le 2M_h < \lambda \le 2\nu \Rightarrow i_\kappa \ne i_\lambda \end{aligned} \tag{3.14c}$$

and for the particles by corresponding relations.

(iii) The Serber function $\Theta^{2\nu}_{S,M,k}$ of the AIP (3.13) is obtained by application of a "t-type" preserving permutation operator $\overline{(\pi_{CS}, \pi_{CS})}^{\sigma}$ (cf. Appendix 1) defined by $(\mathbf{L},\mathbf{I})$ to a Serber function $\Theta^{2\nu}_{S,M,\tilde{k}}$:

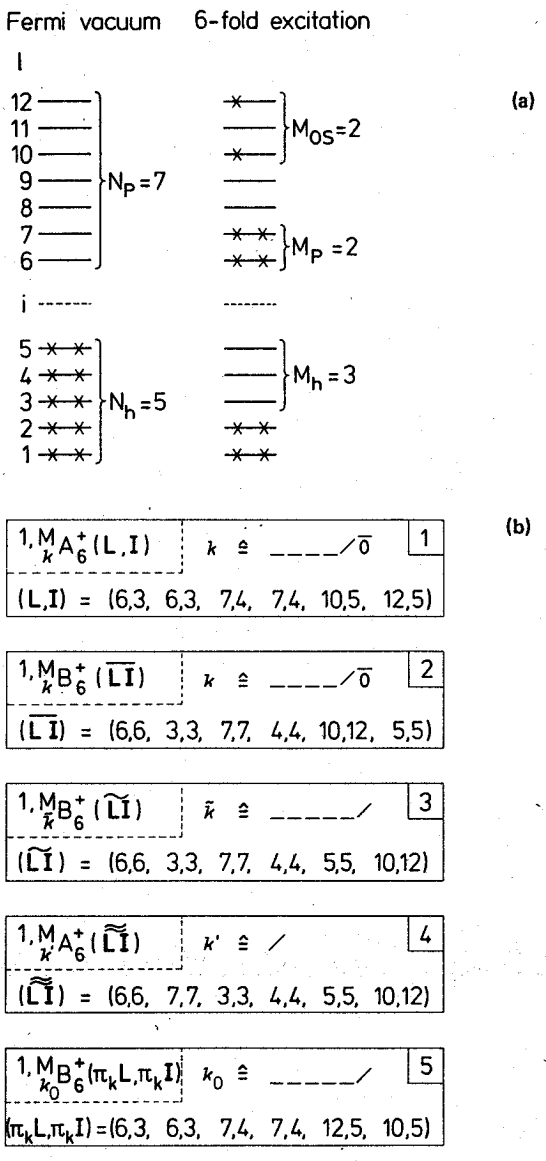

FIG. 1. An illustration for the excitation operators employed in Sec. III. (a) Orbital occupancy pattern for a sample sixfold excitation of a 10 electron system confined to 12 orbitals entailing three hole closed shells ($M_h=3$), two particle closed shells ($M_p=2$), and two particle open shells ($M_{OS}=2$) coupled to a triplet state ($S=1$). (b) Relationships between orbital configurations (OC) and Serber spin coupling routes (SCR); (1) OC and SCR of Eqs. (3.11), (3.13) corresponding to strict particle–hole coupling; (2) OC of Eq. (3.21), the respective SCR being unchanged compared to (1); the excitation operator corresponds to a *pphhpphh* coupling, cf. Eq. (3.23); (3) OC with closed shell and open shell parts separated [Eq. (3.18)], the SCR is defined by Eq. (3.15); SCR and OC result from (2) by a t-type preserving permutation (π_{CS}, π_{CS}) according to Eqs. (3.14d), (3.30); (4) OC with particle closed shells and hole closed shells separated; the SCR refers solely to the open shell part; the corresponding excitation operator is defined in Eq. (3.28); (5) the t-type representative of (1), cf. Eqs. (3.36) and (A1.27).

$$\Theta^{2\nu}_{S,M,k} = \overline{(\pi_{CS}, \pi_{CS})}^{\sigma} \Theta^{2\nu}_{S,M,\tilde{k}} \,. \tag{3.14d}$$

The latter function is of the form

$$\Theta^{2\nu}_{S,M,\tilde{k}} = (\theta_{0,0})^{M_{CS}} \Theta^{M_{OS}}_{S,M,k'} \,, \tag{3.15}$$

where

$$M_{CS} = M_p + M_h \tag{3.16}$$

denotes the total number of closed shells in (L, I) and

$$M_{OS} = 2(\nu - M_{CS}) \tag{3.17}$$

denotes the number of open shells (OS) created by the excitation (3.11). $\Theta^{M_{OS}}_{S,M,k'}$ is one of the $f^{M_{OS}}_S$ (1.16) Serber functions for M_{OS} spin $\frac{1}{2}$ particles and $\theta_{0,0}$ is the geminal singlet function (A1.3a).

The permutation operator $\overline{(\pi_{CS}, \pi_{CS})}^{\sigma}$ is defined by a special permutation $(\pi_{CS}, \pi_{CS}) \in S^{\nu} \times S^{\nu}$ connecting the two orbital configurations $(\widetilde{LI})$ and $(\overline{LI})$

$$(\widetilde{LI}) = [(\pi_{CS}, \pi_{CS})(\overline{LI})] \,. \tag{3.18}$$

The orbital configurations $(\widetilde{LI})$ and $(\overline{LI})$ are both permutations of the configuration (L, I) and are obtained from (L, I) in the following way: Let

$$M_{max} = \max(M_p, M_h) \tag{3.19}$$

and let the permutation $\bar{p} \in S^{2\nu}$

$$\bar{p} = \prod_{\mu=1}^{M_{max}} (4\mu - 2, 4\mu - 1) \tag{3.20}$$

be a M_{max}-fold product of intergeminal transpositions $(4\mu-2, 4\mu-1)$ in the configuration (L, I). $(\overline{LI})$ is then obtained as the permutation $\bar{p}$ of the orbital configuration (L, I)

$$(\overline{LI}) = [\bar{p}(L,I)] \,. \tag{3.21}$$

In $(\overline{LI})$ the ordering of the particle indices is unchanged compared to (L, I). This statement holds for the hole indices alike. *But the phph alternancy of* (L, I) *is destroyed: In* $(\overline{LI})$ *the first* $4M_{max}$ *orbital indices are ordered in a pphhpphh sequence.*

Likewise the permutation (π_{CS}, π_{CS}) creating $(\widetilde{LI})$ from $(\overline{LI})$ does neither destroy the ordering of the particle indices nor that of the hole indices. However, in $(\widetilde{LI})$ only the first $4M_{min}$ orbital indices

$$M_{min} = \min(M_p, M_h) \tag{3.22}$$

are arranged in a *pphh* order. The following $4|\Delta M^{ph}_{CS}|$ orbital indices in $(\widetilde{LI})$ are separated according to whether they are CS or OS indices such that in $(\widetilde{LI})$ the first $2M_{CS}$ orbital indices are all CS indices, while the remaining indices are all OS indices. If, for instance, $\Delta M^{ph}_{CS} > 0$ then the first $4M_h$ CS indices in $(\widetilde{LI})$ are arranged in a *pphh* sequence; they are followed by the remaining $2\Delta M^{ph}_{CS}$ closed shell particle indices which are again followed by $2\Delta M^{ph}_{CS}$ OS hole indices. The remaining orbital indices all correspond to open shells and are ordered in a *phph* sequence. They have not been permuted at all and occupy the same positions as in $(\overline{LI})$ and (L, I).

Thus (π_{CS}, π_{CS}) can be characterized as the permutation which separates in $(\overline{LI})$ CS and OS orbital indices shifting CS index pairs to the left and OS index pairs to the right and preserving thereby the internal order of particles and holes (3.14c), respectively.

C. Geminal creation operators

For the proof of proposition (3.14) we exploit the Serber geminate coupling structure of the AIP's (3.13).

Let $(\widehat{\mathbf{LI}})$ be an arbitrarily ordered orbital configuration of ν particles and ν holes

$$(\widehat{\mathbf{LI}}) = (r_1, \ldots, r_{2\nu}) \tag{3.23a}$$

for which the corresponding AIP

$${}^{S,M}_{k}B^{+}_{\nu}(\widehat{\mathbf{LI}}) = {}^{S,M}_{k}[\mathbf{c}^{+}_{r_1} \wedge \cdots \wedge \mathbf{c}^{+}_{r_{2\nu}}] \tag{3.23b}$$

of irreducible creation operators $\mathbf{c}^{+}_{r} \in \{\mathbf{p}^{+}_{i}, \mathbf{Uh}^{+}_{i}\}$ does not vanish. For the sake of simplicity we introduce the notation

$${}^{S,M}_{k}B^{+}_{\nu}(\widehat{\mathbf{LI}}) = {}^{S,M}_{k}[r^{+}_{1} \cdots r^{+}_{2\nu}] \; . \tag{3.23c}$$

The AIP can be represented as a ν-fold irreducible product of geminal singlet and triplet creation operators ${}^{S}[r^{+}r'^{+}]$. The corresponding reducing transformations are given by (A1.12). There exist three different types of geminal creation operators, the single excitation operators ${}^{S}[l^{+}i^{+}]$, the geminal particle creation operators ${}^{S}[l^{+}m^{+}]$ and the geminal hole creation operators ${}^{S}[i^{+}j^{+}]$. The standard components of these operators are spin-coupled operators of second quantization and can be calculated from the geminal spin functions by virtue of (2.26) and (2.28). The singlet single excitation operator, for instance, is

$$\begin{aligned} {}^{0,0}[l^{+}i^{+}] &= \sqrt{2}\,\overline{A}\,\theta_{0,0}(\mathbf{p}^{+}_{l} \otimes \mathbf{Uh}^{+}_{i}) \\ &= \overline{A}[\alpha(\mathbf{p}^{+}_{l}) \otimes \beta(\mathbf{Uh}^{+}_{i}) - \beta(\mathbf{p}^{+}_{l}) \otimes \alpha(\mathbf{Uh}^{+}_{i})] \\ &= \frac{1}{\sqrt{2}}(p^{+}_{l} \wedge h^{+}_{i} + \overline{p}^{+}_{l} \wedge \overline{h}^{+}_{i}) \\ &= \frac{1}{\sqrt{2}}(p^{+}_{l}h^{+}_{i} + \overline{p}^{+}_{l}\overline{h}^{+}_{i}) \; . \end{aligned} \tag{3.24}$$

The geminal AIP's ${}^{S,M}[r^{+}r'^{+}]$ are normalized spin-coupled operators if $r \neq r'$. For $r = r'$ the triplet operators vanish

$${}^{1,M}[r^{+}r^{+}] = 0 \tag{3.25}$$

whereas the singlet operators ${}^{0,0}[r^{+}r^{+}]$ have the norm 2.

We will denote the *normalized* spin-coupled single excitation operators by ${}^{S,M}S^{+li}$ and the corresponding geminal particle and hole creation operators by ${}^{S,M}P^{+lm}$ and ${}^{S,M}H^{+ij}$, respectively. The following relations hold:

$${}^{S,M}S^{+li} \doteq {}^{S,M}[l^{+}i^{+}] \; , \tag{3.26}$$

$${}^{S,M}P^{+lm} = [1 - \delta_{l,m}(1 - \sqrt{2}\,\delta_{S,0})]^{-1}\,{}^{S,M}[l^{+}m^{+}] \; , \tag{3.27a}$$

$${}^{S,M}H^{+ij} = [1 - \delta_{i,j}(1 - \sqrt{2}\,\delta_{S,0})]^{-1}\,{}^{S,M}[i^{+}j^{+}] \; . \tag{3.27b}$$

Because of (3.25) triplet creation operators (3.27) for $l = m$ and $i = j$ do not exist.

D. An alternative definition of SAAP creation operators

Let ${}^{0}\mathbf{A}$ be a singlet operator and ${}^{S}\mathbf{B}$ an operator of spin multiplicity S. Then according to (2.8) the operator products ${}^{S}\mathbf{B}{}^{0}\mathbf{A}$ and ${}^{0}\mathbf{A}{}^{S}\mathbf{B}$ are again irreducible tensor operators of order S. If ${}^{0,0}A$ and ${}^{S,M}B$ are normalized spin-coupled operators of second quantization (2.23) referring to disjoint orbital sets then their binary products are also normalized.

Because of the anticommutation property of the creation operators (3.7) each orbital index may occur at most twice in the orbital configuration (3.23a) of a spin-coupled ν-fold excitation. Separating OS and CS factors we can therefore *construct* a complete set of SAAP creators in the following way: For the M_{OS} [see (3.17)] open shell creation operators $\mathbf{c}^{+}_{r} \in \{\mathbf{p}^{+}_{i}, \mathbf{Uh}^{+}_{i}\}$ *normalized* spin-coupled operators can be constructed according to (2.24) and (2.25). To the set of the $f^{M_{\mathrm{OS}}}_{S}$ Serber functions $\Theta^{M_{\mathrm{OS}}}_{S,M,k'}$ correspond the operators

$${}^{S,M}_{k'}A^{+}_{M_{\mathrm{OS}}}(\mathrm{OS}) = {}^{S,M}_{k'}[r^{+}_{1} \cdots r^{+}_{M_{\mathrm{OS}}}] \; . \tag{3.28a}$$

The orbital configuration

$$(\mathrm{OS}) = (r_1, \ldots, r_{M_{\mathrm{OS}}}) \tag{3.28b}$$

contains $\nu - 2M_p$ particle indices l_κ and $\nu - 2M_h$ hole indices i_κ. These indices may be arranged in a sequence $i_\kappa < i_{\kappa+1}$ and $l_\kappa < l_{\kappa+1}$. Furthermore, one may arrange particles and holes in such a way, that the last $M_{\mathrm{OS}} - 2|\Delta M^{ph}_{\mathrm{CS}}|$ orbital indices in (OS) occur in a *phph* sequence.

The normalized geminal singlet operators for doubly occupied orbitals are given by (3.27). The total orthonormal SAAP creation operators for the orbital configuration $(\widetilde{\widehat{\mathbf{LI}}})$

$$(\widetilde{\widehat{\mathbf{LI}}}) = (l_1, l_1, \ldots, l_{M_p}, l_{M_p}, i_1, i_1, \ldots, i_{M_h}, i_{M_h}, r_1, \ldots, r_{M_{\mathrm{OS}}}) \tag{3.28c}$$

are then given by the products

$${}^{S,M}_{k'}A^{+}_{\nu}(\widetilde{\widehat{\mathbf{LI}}}) = I(M_p, M_h) \prod_{\mu=1}^{M_p} {}^{0,0}P^{+l_\mu l_\mu} \times \prod_{\lambda=1}^{M_h} {}^{0,0}H^{+i_\lambda i_\lambda}\,{}^{S,M}_{k'}A^{+}_{M_{\mathrm{OS}}}(\mathrm{OS}) \; . \tag{3.28d}$$

The sign

$$I(M_p, M_h) = \pm 1 \tag{3.28e}$$

is defined below. Relations (3.28) represent a definition of the SAAP creators alternative to (3.11).

We will employ the construction (3.28) to prove (3.14a) and define, thereby, the sign $I(M_p, M_h)$. From the commutativity of all geminal creation operators and from (3.27) follows that the excitation operator (3.28) up to a scalar factor is equal to the AIP ${}^{S,M}_{\tilde{k}}B^{+}_{\nu}(\widetilde{\mathbf{LI}})$ defined by the orbital configuration $(\widetilde{\mathbf{LI}})$ (see Sec. 3.3) and the Serber function $\Theta^{2\nu}_{S,M,\tilde{k}}$ [see (3.15)], i.e.,

$${}^{S,M}_{k'}A^{+}_{\nu}(\widetilde{\widehat{\mathbf{LI}}}) = I(M_p, M_h)2^{-M_{\mathrm{CS}}/2}\,{}^{S,M}_{\tilde{k}}B^{+}_{\nu}(\widetilde{\mathbf{LI}}) \; . \tag{3.29}$$

According to (3.18) $(\overline{\mathbf{LI}})$ is obtained from the orbital configuration $(\widetilde{\mathbf{LI}})$ by a permutation $(\pi^{-1}_{\mathrm{CS}}, \pi^{-1}_{\mathrm{CS}})$ in which pairs of CS indices are shifted with respect to pairs of OS indices. Therefore, the corresponding permutation operator $\overline{(\pi_{\mathrm{CS}}, \pi_{\mathrm{CS}})^{\sigma}}$ is a t-type preserving permutation operator which in the Serber function (3.15) shifts the closed shell spin functions with respect to the OS spin geminals collected in $\Theta^{M_{\mathrm{OS}}}_{S,M,k'}$. Applying $\overline{(\pi_{\mathrm{CS}}, \pi_{\mathrm{CS}})^{\sigma}}$ to $\Theta^{2\nu}_{S,M,\tilde{k}}$ one obtains according to Appendix IG a new Serber function $\Theta^{2\nu}_{S,M,k}$ of the same t-type [cf. (3.14d)]. By virtue of (A1.28), (2.31), (2.32), and (3.18) one obtains

$${}^{S,M}_{k}B^{+}_{\nu}(\overline{\mathbf{LI}}) = {}^{S,M}_{\tilde{k}}B^{+}_{\nu}(\widetilde{\mathbf{LI}}) \; . \tag{3.30}$$

Since $\Theta^{2\nu}_{S,M,k}$ is a Serber function, ${}^{S,M}_{k}B^{+}_{\nu}(\overline{\mathbf{LI}})$ is an ir-

reducible product of geminal creation operators. Among these geminal creation operators the last $\nu - 2M_{\max}$ operators are by construction single excitation operators ${}^{S}[l^{+}i^{+}]$. The first $2M_{\max}$ geminal creation operators, due to the *pphh* sequence of the corresponding orbital indices in $(\overline{\mathrm{LI}})$, are pairs of products of geminal particle operators ${}^{S}[l^{+}m^{+}]$ and geminal hole operators ${}^{S}[i^{+}j^{+}]$. For $M_p \geq M_h$ these products are of the form ${}^{0}[l^{+}l^{+}]\,{}^{S}[i^{+}j^{+}]$ and for $M_p \leq M_h$ of the form ${}^{S}[l^{+}m^{+}]\,{}^{0}[i^{+}i^{+}]$. By means of the anticommutation relations (2.5) or using (2.31), (2.32), and (3.25) one can derive the following operator identities:

$${}^{0}[l^{+}l^{+}]\,{}^{S}[i^{+}j^{+}] = -2\,{}^{0}[l^{+}i^{+}]\,{}^{S}[l^{+}j^{+}]\,, \tag{3.31a}$$

$${}^{S}[l^{+}m^{+}]\,{}^{0}[i^{+}i^{+}] = -2\,{}^{S}[l^{+}i^{+}]\,{}^{0}[m^{+}i^{+}]\,. \tag{3.31b}$$

These identities represent the connection between the *pphh* sequence of the first $4M_{\max}$ orbital indices in $(\overline{\mathrm{LI}})$ and the *phph* sequence in (L, I): The application of an intergeminal transposition operator $\overline{(4\mu-2, 4\mu-1)}^{\nu}$, where $1 \leq \mu \leq M_{\max}$, to the AIP ${}^{S,M}_{k}B^{+}(\overline{\mathrm{LI}})$ yields an AIP defined by the permuted orbital configuration but by the same spin function multiplied by a factor -2. From (3.20) and (3.21) we obtain then

$${}^{S,M}_{k}B^{+}_{\nu}(\overline{\mathrm{LI}}) = (-2)^{M_{\max}}\,{}^{S,M}_{k}B^{+}_{\nu}(\mathrm{L,I})\,. \tag{3.32}$$

If we define now

$$I(M_p, M_h) = (-1)^{M_{\max}} \tag{3.33}$$

then Eqs. (3.14b), (3.16), (3.19), and (3.29)–(3.33) are summarized by

$${}^{S,M}_{k'}A^{+}_{\nu}(\widetilde{\overline{\mathrm{LI}}}) = 2^{\lfloor \Delta M^{ph}_{\mathrm{CS}}/2 \rfloor}\,{}^{S,M}_{k}B^{+}_{\nu}(\mathrm{L,I})\,. \tag{3.34}$$

This verifies that (3.14a) gives indeed the proper normalization constant for the irreducible product ${}^{S,M}_{k}B^{+}_{\nu}(\mathrm{L,I})$ of single excitations ${}^{S}[l^{+}i^{+}]$.

E. Dimension of the spin-adapted ν-fold excitation space

Let ${}^{S}\mathbf{A}^{(\nu)} \subset \tilde{\mathbf{A}}^{(\nu)}$ denote the subspace of the ν-fold excitations of spin S. ${}^{S}\mathbf{A}^{(\nu)}$ is contained $(2S+1)$ times in $\tilde{\mathbf{A}}^{(\nu)}$ and it follows from (3.28)

$$\dim {}^{S}\mathbf{A}^{(\nu)} = \sum_{M_p, M_h=0}^{\mu} f_{S}^{M_{\mathrm{OS}}} \binom{N_h}{\nu - M_h} \binom{N_p}{\nu - M_p} \binom{\nu - M_h}{M_h} \binom{\nu - M_p}{M_p} \tag{3.35a}$$

with

$$\mu = \begin{cases} \nu/2 & \text{if } \nu \text{ even} \\ (\nu-1)/2 & \text{if } \nu \text{ odd} \end{cases} \tag{3.35b}$$

and

$$0 \leq M_p + M_h \leq \nu - S\,. \tag{3.35c}$$

$f_{S}^{M_{\mathrm{OS}}}$ is given by (1.16) and (3.17), N_h and N_p are the total numbers of occupied and unoccupied orbitals referring to the Fermi vacuum and M_p and M_h are the numbers of particle and hole CS's, respectively, created by the excitation.

Consider for example a system of 8 electrons in a minimum orbital basis, i.e., $N_p = N_h = 4$. The dimension of the space of all quadruple excitations $\tilde{\mathbf{A}}^{(4)}$ according to (3.8) is equal to 4900, the dimension of the singlet subspace ${}^{0}\mathbf{A}^{(4)}$ is 626. This illustrates the advantage arising from the use of the spin-adapted wave functions.

F. Representatives for the Serber coupled ν-fold excitations

We will show now how the SAAP creators expressed by ν-fold irreducible products of spin-coupled single excitations can be reduced to a subset of class representatives.

In Appendix IF–IG the set of Serber functions $\Theta^{2\nu}_{S,M,k}$ had been divided into $f^{2\nu}_{ST}$ (A1.23) equivalence classes $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$ of the same t-type $\underline{k}$ and every function had been expressed through its class representative. This division of the Serber functions into classes induces a division of the corresponding AIP's ${}^{S,M}_{k}B^{+}_{\nu}(\mathrm{L,I})$ (3.13) into corresponding equivalence classes. An AIP ${}^{S,M}_{k_0}B^{+}_{\nu}(\mathrm{L,I})$ is called a representative of such a class if the corresponding Serber function $\Theta^{2\nu}_{S,M,k_0}$ is the representative of the class $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$. Furthermore, we say that ${}^{S,M}_{k}B^{+}_{\nu}(\mathrm{L,I})$ is of t-type $\underline{k}$ if the corresponding Serber function is of this t-type.

Let now ${}^{S,M}_{k}B^{+}_{\nu}(\mathrm{L,I})$ be of t-type $\underline{k}$ and let $\overline{(\pi_k, \pi_k)}^{\sigma}$ be the t-type preserving permutation operator which creates the corresponding Serber function from its representative. By virtue of (A1.13), (A1.14), (A1.28), (2.31), and (2.33)

$${}^{S,M}_{k}B^{+}_{\nu}(\mathbf{L,I}) = {}^{S,M}_{k_0}B^{+}_{\nu}(\pi_k\mathbf{L}, \pi_k\mathbf{I})\,, \tag{3.36a}$$

where

$$(\pi_k\mathbf{L}, \pi_k\mathbf{I}) = (l_{\pi_k(1)}, i_{\pi_k(1)}, \ldots, l_{\pi_k(\nu)}, i_{\pi_k(\nu)})\,, \tag{3.36b}$$

i.e., the excitation operator ${}^{S,M}_{k}B^{+}_{\nu}$ for the orbital configuration (L, I) is equal to the t-type representative ${}^{S,M}_{k_0}B^{+}_{\nu}$ for the permuted configuration $(\pi_k\mathbf{L}, \pi_k\mathbf{I})$.

G. Summary and discussion of the SAAP basis construction

To represent the SAAP creation operators ${}^{S,M}_{k'}A^{+}_{\nu}(\widetilde{\overline{\mathrm{LI}}})$ given in (3.28) by the t-type representatives ${}^{S,M}_{k_0}B^{+}_{\nu}(\pi_k\mathbf{L}, \pi_k\mathbf{I})$ one proceeds as follows:

(i) In the first step the CS special cases are considered. If $(\widetilde{\overline{\mathrm{LI}}})$ contains no CS then $(\widetilde{\overline{\mathrm{LI}}}) = (\mathrm{L,I})$ and $k' = \bar{k} = k$. Otherwise $\bar{k}$ follows from k' according to (3.15) and k from $\bar{k}$ according to (3.14d) by means of the permutation $(\pi^{-1}_{\mathrm{CS}}, \pi^{-1}_{\mathrm{CS}})$. This permutation is different from the identity (e, e), i.e., $k \neq \bar{k}$, if

$$M_p - M_h \neq 0, 1\,. \tag{3.37}$$

In this case $(\pi^{-1}_{\mathrm{CS}}, \pi^{-1}_{\mathrm{CS}})$ is defined as the permutation of $(\widetilde{\overline{\mathrm{LI}}})$ [or equivalently of $(\widetilde{\overline{\mathrm{LI}}})$; cf. (3.29)] which mixes CS index pairs among OS index pairs such that a *pphh* sequence is created for orbital indices neither in a *pphh* nor in a *phph* sequence. To each pair (M_p, M_h) there is exactly one such permutation $(\pi^{-1}_{\mathrm{CS}}, \pi^{-1}_{\mathrm{CS}}) \in S^{\nu} \times S^{\nu}$. Let for instance

$$(\widetilde{\overline{\mathrm{LI}}}) = (l_1, l_1, l_3, l_3, i_1, i_2, i_3, i_4, l_5, i_5)$$

be the orbital configuration of a five-fold excitation con-

taining two particle CS. Then π_{CS}^{-1} is the neighbor transposition $(23) \in S^5$ which yields

$$(\overline{\mathbf{L}\mathbf{I}}) = (l_1, l_1, i_1, i_2, l_3, l_3, i_3, i_4, l_5, i_5) .$$

The genealogy symbol k is obtained from k' and π_{CS}^{-1} most simply through a consideration of the corresponding coupling routes in the Serber branching diagram Fig. 3. If, in our example, k' corresponds to /_, then $\tilde{k}$ corresponds to _/_ and k corresponds to _/$\bar{0}$_ as (3.14d) reads

$$\_/\bar{0}\backslash\_ = \overline{(23)}\_/\backslash\_ .$$

In this way each pair (M_p, M_h) uniquely defines a mapping $\overline{\mathbf{M}_p}, \overline{\mathbf{M}_h}$ of the set of Serber functions $\mathbf{C}_{S,M}^{M_{OS}}$ (A1.18) into the set $\mathbf{C}_{S,M}^{2\nu}$ such that $\overline{\mathbf{M}_p}, \overline{\mathbf{M}_h}(k') = k$. In the above example $\overline{\mathbf{M}_p}, \overline{\mathbf{M}_h} = \overline{2,0}$ and $\overline{2,0}(/\backslash\_) = \_/\bar{0}\backslash\_$. Having determined for a given degree of excitation ν and spin multiplicity S all nontrivial mappings [these are characterized by all pairs (M_p, M_h) satisfying the conditions (3.37), (3.35c), $M_p + M_h > 0$, $M_p \leq \mu$, and $M_h \leq \mu$, μ being defined by (3.35b)], each SAAP creator can be represented by virtue of (3.14a) as an AIP of particle–hole (ph) creation operators. This AIP is then defined by an orbital configuration (L, I) and one of the $f_S^{2\nu}$ spin functions which span the dual representation $[\nu+S, \nu-S]$.

(ii) In the second step one needs to determine the permutation $\pi_k^{-1} \in S^\nu$ which maps each ν-fold excitation operator ${}^{S,M}_{k}B_\nu^\dagger(\mathbf{L}, \mathbf{I})$ according to (3.36) on the t-type representative ${}^{S,M}_{k_0}B_\nu^\dagger(\pi_k\mathbf{L}, \pi_k\mathbf{I})$. π_k^{-1} is defined by (A1.27). If, as in our example,

$$(\mathbf{L}, \mathbf{I}) = (l_1, i_1, l_1, i_2, l_3, i_3, l_3, i_4, l_5, i_5) \quad \text{and} \quad k \hat{=} \_/\bar{0}\backslash\_ ,$$

then k_0 corresponds to ___/\; consequently π_k is the 4-cycle (2453) and the permuted configuration is given by

$$(\pi_k\mathbf{L}, \pi_k\mathbf{I}) = (l_1, i_1, l_3, i_3, l_5, i_5, l_1, i_2, l_3, i_4) .$$

For the characterization of all possible SAAP creators in terms of AIP's of ph creation operators corresponding to the orbital configuration (L, I) all $f_S^{2\nu}$ spin functions are needed. However, employing the permuted orbital configurations $(\pi_k\mathbf{L}, \pi_k\mathbf{I})$ for the definition of the SAAP creators only the $f_{ST}^{2\nu}$ class representatives $\Theta_{S,M,k_0}^{2\nu}$ are needed for a complete characterization of all SAAP creators. This leads to a reduction of the dimension of the representation matrices of $S^{2\nu}$ as one can expand the CI-Hamiltonian in terms of AIP's (3.13) expressed by few class representatives. Thus, we will show in the next section that the evaluation of all possible CI-matrix elements requires only $f_{ST}^{2\nu}$-dimensional submatrices of the $f_S^{2\nu}$-dimensional representation matrices of $S^{2\nu}$.

IV. MATRIX ELEMENTS OF THE $2N_h$ ELECTRON HAMILTONIAN

To determine the matrix elements of the $2N_h$ electron Hamiltonian $\hat{H}$ [Eq. (2.7)] in the SAAP basis we introduce an appropriate representation of $\hat{H}$ in terms of geminal, normalized, spin-coupled operators of second quantization.

A. Representation of $\hat{H}$ by spin-adapted particle-hole operators

$\hat{H}$ can be expressed in terms of the following ITO's, the *particle shift operator*

$${}^{S}\mathbf{P}_m^{+l} = {}^{S}[\mathbf{p}_l^\dagger \mathbf{U} \mathbf{p}_m] , \tag{4.1a}$$

the *hole shift operator*

$${}^{S}\mathbf{H}_j^{+l} = {}^{S}[\mathbf{U}\mathbf{h}_l^\dagger \mathbf{h}_j] , \tag{4.1b}$$

the *deexcitation operator*

$${}^{S}\mathbf{S}_{il} = {}^{S}[\mathbf{h}_l \mathbf{U} \mathbf{p}_i] , \tag{4.2}$$

and the *excitation operator* [Eq. (3.26)] ${}^{S}\mathbf{S}^{+il}$. Expression (4.2) is the conjugate of the latter operator and can be constructed as the AIP of the corresponding annihilation operators, i.e., ${}^{S}[il] = {}^{S}[\mathbf{h}_l \wedge \mathbf{U}\mathbf{p}_i]$. The standard components of the operators (4.1) are normalized spin-coupled operators of second quantization determined by means of the spin mapping (2.29).

For the following it is useful to assume the customary notations for the matrix elements of the one-particle and two-particle operators in the orbital basis (1.23)

$$z_{rr'} = \langle \phi_r | \hat{z} | \phi_{r'} \rangle , \tag{4.3a}$$

$$(r_1 r_3 | r_2 r_4) = \langle \phi_{r_1} \phi_{r_2} | \hat{v}_{12} | \phi_{r_3} \phi_{r_4} \rangle . \tag{4.3b}$$

Furthermore, we define

$$E_0 = \sum_{i=1}^{N_h} \left\{ 2z_{ii} + \sum_{j=1}^{N_h} [2(ii|jj) - (ij|ij)] \right\} \tag{4.4a}$$

$$F_{rr'} = z_{rr'} + \sum_{j=1}^{N_h} [2(jj|rr') - (rj|r'j)] . \tag{4.4b}$$

By virtue of the anticommutation relations (2.5) one can show that $\hat{H}$ can be decomposed into a sum of operators $\hat{H}_\eta$

$$\hat{H} = \sum_{\eta=-2}^{+2} \hat{H}_\eta . \tag{4.5a}$$

$\hat{H}_\eta$, when applied to a ν-fold excitation, changes the degree ν of this excitation by η mapping it onto a linear combination of $(\nu+\eta)$-fold excitations. The $\hat{H}_\eta$ are given by the following expansions of spin-coupled operators (4.1), (4.2), and (3.26)

$$\hat{H}_{+2} = \sum_{l,m,i,j} (li|mj)\, {}^{0,0}\mathbf{S}^{+li}\, {}^{0,0}\mathbf{S}^{+mj} \tag{4.5b}$$

$$\hat{H}_{+1} = \sqrt{2} \sum_{l,i} \left[F_{li}\, {}^{0,0}\mathbf{S}^{+li} + \sqrt{2} \sum_{m,n} (li|mn)\, {}^{0,0}\mathbf{S}^{+li}\, {}^{0,0}P_n^{+m} + \sqrt{2} \sum_{j,k} (li|jk)\, {}^{0,0}\mathbf{S}^{+li}\, {}^{0,0}H_k^{+j} \right] \tag{4.5c}$$

$$\hat{H}_0 = E_0 + \sqrt{2} \left(\sum_{l,m} F_{lm}\, {}^{0,0}P_m^{+l} + \sum_{i,j} F_{ij}\, {}^{0,0}H_j^{+i} \right) + \sum_{l,m,n} \left[\sum_o (lm|no)\, {}^{0,0}P_o^{+n} - \frac{1}{\sqrt{2}} (ln|mn) \right] {}^{0,0}P_m^{+l}$$
$$+ \sum_{i,j,g} \left[\sum_k (ij|gk)\, {}^{0,0}H_k^{+g} + \frac{1}{\sqrt{2}} (ig|jg) \right] {}^{0,0}H_j^{+i} + 2 \sum_{l,m,i,j} [(lm|ij)\, {}^{0,0}P_m^{+l}\, {}^{0,0}H_j^{+i} + (li|mj)\, {}^{0,0}\mathbf{S}^{+li}\, {}^{0,0}\mathbf{S}_{jm}] . \tag{4.5d}$$

The operators $\hat{H}_{-\eta}$ are the conjugates of the operators $\hat{H}_{\eta}$. Equations (4.5b)–(4.5d) may be summarized by the operator expansion

$$\hat{H}_{\eta}=\sum_{\zeta} c_{\eta\zeta}\hat{H}_{\eta\zeta}\ , \tag{4.5e}$$

where the $\hat{H}_{\eta\zeta}$ belong to the following classes of singlet operators (I is the identity operator)

$$\{I,\ {}^{0,0}S^{+ii},\ {}^{0,0}S^{+ii}\ {}^{0,0}S^{+mj}\} \tag{4.5f}$$

$$\{{}^{0,0}P^{+i}_{m},\ {}^{0,0}H^{+i}_{j},\ {}^{0,0}S^{+ii}\ {}^{0,0}H^{+j}_{k},\ {}^{0,0}S^{+ii}\ {}^{0,0}P^{+m}_{n},$$
$${}^{0,0}H^{+g}_{k}\ {}^{0,0}H^{+i}_{j},\ {}^{0,0}P^{m}_{o}\ {}^{0,0}P^{+i}_{m},\ {}^{0,0}P^{+i}_{m}\ {}^{0,0}H^{+i}_{j}\} \tag{4.5g}$$

$$\{{}^{0,0}S^{+ii}\ {}^{0,0}S_{jm}\}\ . \tag{4.5h}$$

The operators of the class (4.5f) contain no annihilation operators at all, the operators of the class (4.5g) contain such operators only as parts of the particle and hole shift operators (4.1) and the last class contains particle and hole annihilation operators as parts of singlet de-excitation operators (4.2).

B. The action of the Hamiltonian on the SAAP creation operator

Every SAAP creation operator ${}^{S,M}_{k}A^{+}_{\nu}$ [Eq. (3.11)] can be represented as an AIP [see Eq. (3.13)] of ph creation operators by means of a normalization constant K given by Eq. (3.14a). The calculation of matrix elements of SAAP creation operators can then be reduced to the calculation of the matrix elements of the corresponding AIP's ${}^{S,M}_{k}B^{+}_{\nu}$

$$\langle {}^{S_1,M_1}_{k_1}A^{+}_{\nu_1}|\hat{H}|{}^{S_2,M_2}_{k_2}A^{+}_{\nu_2}\rangle = K_1K_2\langle {}^{S_1,M_1}_{k_1}B^{+}_{\nu_1}|\hat{H}|{}^{S_2,M_2}_{k_2}B^{+}_{\nu_2}\rangle\ . \tag{4.6a}$$

We have used the notation

$$|{}^{S,M}_{k}A^{+}_{\nu}\rangle = {}^{S,M}_{k}A^{+}_{\nu}||0\rangle\rangle\ . \tag{4.6b}$$

The action of the operators $\hat{H}_{\eta\zeta}$ on excitation operators ${}^{S,M}_{k}B^{+}_{\nu}$ is readily determined. Since the $\hat{H}_{\eta\zeta}$ are *singlet* operators the operator products $\hat{H}_{\eta\zeta}\ {}^{S,M}_{k}B^{+}_{\nu}$ are standard components of ITO's of order S. They create $(\nu+\eta)$-fold excited, spin adapted, antisymmetrized functions from the Fermi vacuum $||0\rangle\rangle$. For the Hamiltonian matrix elements one finds by means of the Wigner–Eckart theorem and by means of the orthogonality of the excitation spaces $\tilde{\mathbf{A}}^{(\nu_1)}$ and $\tilde{\mathbf{A}}^{(\nu_2)}$ for $\nu_1\neq\nu_2$

$$\langle {}^{S_1,M_1}_{k_1}B^{+}_{\nu_1}|\hat{H}|{}^{S_2,M_2}_{k_2}B^{+}_{\nu_2}\rangle = \delta_{\nu_1,\nu_2+\eta}\delta_{S_1,S_2}\delta_{M_1,M_2}\sum_{\zeta}c_{\eta\zeta}\langle {}^{S_1,M_1}_{k_1}B^{+}_{\nu_1}|\hat{H}_{\eta\zeta}\ {}^{S_1,M_1}_{k_2}B^{+}_{\nu_2}\rangle\ . \tag{4.7}$$

The functions $|\hat{H}_{\eta\zeta}\ {}^{S,M}_{k}B^{+}_{\nu}\rangle$ in (4.7) are linear combinations of $(\nu+\eta)$-fold excited functions $|{}^{S,M}_{\zeta\tilde{k}}B^{+}_{\nu+\eta}\rangle$ created by AIP's (3.13) of ph creation operators

$$\hat{H}_{\eta\zeta}\ {}^{S,M}_{k}B^{+}_{\nu}||0\rangle\rangle = \sum_{\tilde{k}} D_{\zeta\tilde{k}}\ {}^{S,M}_{\zeta\tilde{k}}B^{+}_{\nu+\eta}||0\rangle\rangle\ . \tag{4.8}$$

For the nontrivial cases the proof of (4.8) and the derivation of the coefficients $D_{\zeta\tilde{k}}$ is given in Appendix II. For the operators $\hat{H}_{\eta\zeta}$ of class (4.5f) the statement (4.8) is obvious since in this case the operator products $\hat{H}_{\eta\zeta}\ {}^{S,M}_{k}B^{+}_{\nu}$ are already $(\nu+\eta)$-fold excited AIP's of ph creators. We denote these operators by

$${}^{S,M}_{\tilde{k}}B^{+}_{\nu+1}(mj) = {}^{0,0}S^{+mj}\ {}^{S,M}_{k}B^{+}_{\nu}\ , \tag{4.9a}$$

$${}^{S,M}_{\tilde{\tilde{k}}}B^{+}_{\nu+2}(limj) = {}^{0,0}S^{+ii}\ {}^{S,M}_{\tilde{k}}B^{+}_{\nu+1}(mj)\ . \tag{4.9b}$$

If ${}^{S,M}_{k}B^{+}_{\nu}$ is defined by the orbital configuration (3.12) and the Serber function $\Theta^{2\nu}_{S,M,k}$ then the operator ${}^{S,M}_{\tilde{k}}B^{+}_{\nu+1}(mj)$ corresponds to the orbital configuration $(m, l_1, \ldots, l_\nu, j, i_1, \ldots, i_\nu)$ and to the Serber function

$$\Theta^{2(\nu+1)}_{S,M,\tilde{k}} = \theta_{0,0}\Theta^{2\nu}_{S,M,k}\ . \tag{4.9c}$$

The operators $\hat{H}_{\eta\zeta}$ of the remaining classes (4.5g) and (4.5h) annihilate the Fermi vacuum. From the identity

$$\hat{H}_{\eta\zeta}\ {}^{S,M}_{k}B^{+}_{\nu} = [\hat{H}_{\eta\zeta},\ {}^{S,M}_{k}B^{+}_{\nu}] + {}^{S,M}_{k}B^{+}_{\nu}\hat{H}_{\eta\zeta} \tag{4.10}$$

follows that the action of the products $\hat{H}_{\eta\zeta}\ {}^{S,M}_{k}B^{+}_{\nu}$ on the Fermi vacuum is determined by the commutators of the $\hat{H}_{\eta\zeta}$ with the AIP's of ph creation operators. In Appendix II it is shown that, up to operators annihilating the Fermi vacuum, these commutators are presented by linear combinations of $(\nu+\eta)$-fold excitation operators (3.13).

From these results and from the decomposition (4.5) of the Hamiltonian one obtains

$$\hat{H}_{\eta}\ {}^{S,M}_{k}B^{+}_{\nu}||0\rangle\rangle = \sum_{\zeta}c_{\eta\zeta}\sum_{\tilde{k}}D_{\zeta\tilde{k}}\ {}^{S,M}_{\zeta\tilde{k}}B^{+}_{\nu+\eta}||0\rangle\rangle \tag{4.11a}$$

and more explicitly

$$\hat{H}_{+2}\ {}^{S,M}_{k}B^{+}_{\nu}||0\rangle\rangle = \sum_{l,m,i,j}(li|mj)\ {}^{S,M}_{\tilde{\tilde{k}}}B^{+}_{\nu+2}(limj)||0\rangle\rangle \tag{4.11b}$$

$$\hat{H}_{+1}\ {}^{S,M}_{k}B^{+}_{\nu}||0\rangle\rangle = \sqrt{2}\sum_{l,i}\Big(F_{li}\ {}^{S,M}_{\tilde{k}}B^{+}_{\nu+1}(li) + \sum_{\mu=1}^{\nu}\Big\{\sum_{m}(li|ml_\mu)\ {}^{S,M}_{\tilde{\tilde{k}}}B^{+}_{\nu+1}(li,(m,l_\mu))$$
$$-\sum_{j}(li|ji_\mu)\ {}^{S,M}_{\tilde{\tilde{k}}}B^{+}_{\nu+1}(li,(j,i_\mu))\Big\}\Big)||0\rangle\rangle \tag{4.11c}$$

$$\hat{H}_{0}\ {}^{S,M}_{k}B^{+}_{\nu}||0\rangle\rangle = \Big(E_0\ {}^{S,M}_{k}B^{+}_{\nu} + \sum_{\mu=1}^{\nu}\Big[\sum_{m}F_{ml_\mu}\ {}^{S,M}_{k}B^{+}_{\nu}(m,l_\mu) - \sum_{j}F_{ji_\mu}\ {}^{S,M}_{k}B^{+}_{\nu}(j,i_\mu)\Big] + \sum_{\mu<\lambda}\Big\{\sum_{l,n}(ll_\mu|nl_\lambda)\ {}^{S,M}_{k}B^{+}_{\nu}((l,l_\mu),(n,l_\lambda))$$
$$+\sum_{i,g}(ii_\mu|gi_\lambda)\ {}^{S,M}_{k}B^{+}_{\nu}((i,i_\mu),(g,i_\lambda))\Big\} + \sum_{\mu,\lambda}\sum_{l,i}\Big\{2(li|l_\mu i_\lambda)\sum_{k_0=1}^{f^{2\nu}_{3T}}\sum_{\pi_{k'}\in T(k_0)}K^{S2\nu}_{k_0k}(\pi_{k'}\mu,\pi_{k'}\lambda)(\overline{\pi_{k'}\mu,\pi_{k'}\lambda})^{r-1}$$
$$*\ {}^{S,M}_{k_0}B^{+}_{\nu}((l,l_\mu),(i,i_\lambda)) - (ll_\mu|ii_\lambda)\ {}^{S,M}_{k}B^{+}_{\nu}((l,l_\mu),(i,i_\lambda))\Big\}\Big)||0\rangle\rangle \tag{4.11d}$$

In (4.11) the following definitions [Eqs. (4.12)–(4.15) below] have been used in addition to Eq. (4.9):

(i) A pair (m, l_μ) of orbital indices as an argument of an AIP indicates that in the corresponding orbital configuration (3.12) the orbital index l_μ, $\mu \in \{1, \ldots, \nu\}$, has been replaced by the orbital index m. For instance,

$$ {}^{S,M}_{k}B^{+}_{\nu}(m, l_\mu) = {}^{S,M}_{k}[l_1^+ i_1^+ \cdots m^+ i_\mu^+ \cdots l_\nu^+ i_\nu^+] \, . \tag{4.12} $$

(ii) The permutation operator $(\overline{\pi_{k'}\mu, \pi_{k'}\lambda})^r$ in (4.11d) is a product of two permutation operators of $\overline{S}^\nu \times \overline{S}^\nu$

$$ (\overline{\pi_{k'}\mu, \pi_{k'}\lambda})^r = (\overline{\pi_{k'}, \pi_{k'}})^r (\overline{\mu, \lambda})^r \, . \tag{4.13} $$

The permutation operator $(\overline{\mu, \lambda})^r$ is defined by the two cyclic permutations

$$ \mu = (12 \cdots \mu) \quad \text{and} \quad \lambda = (12 \cdots \lambda) \tag{4.14} $$

of S^ν [cf. Appendix II]. The permutation operator $(\overline{\pi_{k'}, \pi_{k'}})^r$ is the t-type preserving permutation operator which maps the AIP ${}^{S,M}_{k'}B^{+}_{\nu}$ on its t-type representative ${}^{S,M}_{k_0}B^{+}_{\nu}$ [cf. (2.31) and (3.36)]. From the set of all such permutation operators $\overline{T(k_0)} \times \overline{T(k_0)}$ one can create the whole class of AIP's of t-type k_0 (cf. Appendix IG). Thus the double sum in (4.11d), where the first sum runs over all $f^{2\nu}_{ST}$ classes and the second sum runs for each class over the class creating permutations, represents the sum over all $f^{2\nu}_{S}$ coupling routes k' of the irreducible Serber representation $[\nu+S, \nu-S]$ of $S^{2\nu}$.

(iii) The coefficients $K^{S\,2\nu}_{k_0 k}(\pi_{k'}\mu, \pi_{k'}\lambda)$ in (4.11d) are given by the Serber matrix $\mathbf{U}^{S\,2\nu}$ representing the permutation $(\pi_{k'}\mu, \pi_{k'}\lambda) \in S^\nu \times S^\nu$ and by the projector $\tau(k')$ defined by the Serber matrix element $U^{S\,2\nu}_{k'k'}(12)$ of intrageminal transposition (12) of the first geminal pair

$$ K^{S\,2\nu}_{k_0 k}(\pi_{k'}\mu, \pi_{k'}\lambda) = U^{S\,2\nu}_{k_0 k}(\pi_{k'}\mu, \pi_{k'}\lambda)\tau(k') \tag{4.15a} $$

$$ \tau(k') = \tfrac{1}{2}[1 + U^{S\,2\nu}_{k'k'}(12)] \, . \tag{4.15b} $$

From (1.21) and (A1.29) one finds $\tau(k') = 1$ if the first geminal pair of $\Theta^{2\nu}_{S,M,k'}$ is a singlet spin pair, and $\tau(k') = 0$ otherwise. The coefficients (4.15a) contribute to the sum over all k' in (4.11d) only in the first case, i.e., $\tau(k') = 1$.

According to (4.11) all the AIP's ${}^{S,M}_{\zeta k}B^{+}_{\nu+\eta}$ are t-type representatives, if the AIP ${}^{S,M}_{k}B^{+}_{\nu}$ from which they are created by $\hat{H}_\eta$ is also a t-type representative. Since one can express each SAAP creator by a t-type representative we conclude from a comparison of (4.6a), (4.7), and (4.11) that the SAAP matrix element calculation has been reduced to the calculation of scalar products between t-type representatives of ν-fold excitation operators.

C. Scalar products of AIP's of *ph* creation operators

Let the two ν-fold excitation operators (3.13) ${}^{S,M}_{k}B^{+}_{\nu}(\mathbf{L}, \mathbf{I})$ and ${}^{S,M}_{k'}B^{+}_{\nu}(\mathbf{M}, \mathbf{J})$ correspond to the *orbital configurations*

$$ (\mathbf{L}, \mathbf{I}) = (l_1, i_1, \ldots, l_\nu, i_\nu) $$

and

$$ (\mathbf{M}, \mathbf{J}) = (m_1, j_1, \ldots, m_\nu, j_\nu) \, , \tag{4.16} $$

respectively. According to (2.37) their scalar product is given by

$$ \langle {}^{S,M}_{k}B^{+}_{\nu}(\mathbf{L}, \mathbf{I}) \big| {}^{S,M}_{k'}B^{+}_{\nu}(\mathbf{M}, \mathbf{J}) \rangle = \sum_{p \in S^{2\nu}} U^{S\,2\nu}_{kk'}(p)\delta(l_1 i_1 \cdots l_\nu i_\nu, m_{p(1)} j_{p(1)} \cdots m_{p(\nu)} j_{p(\nu)}) \, . \tag{4.17} $$

All those permutations which destroy the *phph* alternancy in $(\mathbf{M}, \mathbf{J})$ do not contribute to this sum. Thus the sum reduces to those permutations which separately permute particles and holes among each other, i.e., to the permutations (p_m, p_j) of the subgroup $S^\nu \times S^\nu$ [cf. Appendix I E].

The orbital configurations (4.16) define the *index sets*

$$ \mathbf{L} = \{l_1, l_2, \ldots, l_\nu\} \, , \quad \mathbf{I} = \{i_1, i_2, \ldots, i_\nu\} \tag{4.18a} $$

and

$$ \mathbf{M} = \{m_1, m_2, \ldots, m_\nu\} \, , \quad \mathbf{J} = \{j_1, j_2, \ldots, j_\nu\} \, . \tag{4.18b} $$

The scalar product (4.17) may be different from zero only if these index sets are identical

$$ \mathbf{L} = \mathbf{M} \quad \text{and} \quad \mathbf{I} = \mathbf{J} \, . \tag{4.19} $$

In the sets $\mathbf{M}$ and $\mathbf{J}$ each orbital index may occur at most twice. If there are M_p and M_h such CS indices in $\mathbf{M}$ and $\mathbf{J}$, respectively, then there are 2^{M_p} permutations $p_m \in S^\nu$ and 2^{M_h} permutations $p_j \in S^\nu$ for which [if (4.19) holds]

$$ \delta(l_1 \cdots l_\nu, m_{p_m(1)} \cdots m_{p_m(\nu)}) = 1 \, , \tag{4.20a} $$

$$ \delta(i_1 \cdots i_\nu, j_{p_j(1)} \cdots j_{p_j(\nu)}) = 1 \, . \tag{4.20b} $$

This can be seen from the following consideration:

Let p_{m_0} and p_{j_0} be permutations of S^ν such that (4.20) is valid. If the M_p-fold direct product $(\times S^2)^{M_p}$ is the subgroup of S^ν permuting identical particle indices among each other and if $(\times S^2)^{M_h}$ is the corresponding permutation group for the hole indices, then the elements of S^ν for which (4.20) is valid are the elements of the right cosets

$$ S^\nu_{m_0} = (\times S^2)^{M_p} p_{m_0} \tag{4.21a} $$

$$ S^\nu_{j_0} = (\times S^2)^{M_h} p_{j_0} \, . \tag{4.21b} $$

These cosets have 2^{M_p} and 2^{M_h} elements.

Summarizing we can state that in (4.17) $2^{M_p+M_h}$ representation matrix elements of permutations (p_m, p_j) of the subgroup $S^\nu \times S^\nu$ have to be summed up. Thus, the nonzero scalar products [for which condition (4.19) must hold] are given by

$$ \langle {}^{S,M}_{k}B^{+}_{\nu}(\mathbf{L}, \mathbf{I}) \big| {}^{S,M}_{k'}B^{+}_{\nu}(\mathbf{M}, \mathbf{J}) \rangle = \sum_{(p_m, p_j) \in S^\nu_{m_0} \times S^\nu_{j_0}} U^{S\,2\nu}_{kk'}(p_m, p_j) \, . \tag{4.22} $$

To calculate all possible scalar products (4.22) of ν-fold excitations (3.13) defined by arbitrary orbital configurations (4.16), all $(\nu!)^2$ Serber representation matrices $\mathbf{U}^{S\,2\nu}(p_m, p_j)$ are needed. Since these matrices according to (1.21) and (A1.30) exhibit the "even–odd" symmetry

$$ U^{S\,2\nu}_{kk'}(p_m, p_j) = \alpha_0(k)\alpha_0(k')U^{S\,2\nu}_{kk'}(p_j, p_m) \, , \tag{4.23} $$

only $\nu!(\nu!+1)/2$ representation matrix elements and $f^{2\nu}_{ST}$ "parities" $\alpha_0(k)$ have to be stored as parameters for the scalar product calculation (cf. Appendix II).

D. Matrix element formulas

With Eqs. (4.6a), (4.7), (4.11), and (4.22) the problem of the calculation of SAAP matrix elements of the Hamiltonian has been solved in principle. However, as shown by a comparison of equations (4.6a), (4.7), and (4.11) for the calculation of a single matrix element of a $(\nu+\eta)$-fold and a ν-fold excited SAAP one needs to carry out *extended summations over all occupied and unoccupied orbitals*. Taking proper account of condition (4.19) *these sums can be reduced a priori to the few nonvanishing terms*. This reduction will be carried out now.

We first conclude from (4.11), that the operators $\hat{H}_{\eta\zeta}$ acting on a ν-fold excitation $|{}^{S,M}_{k_2}B^+_\nu\rangle$ with index sets

$$\mathbf{L}=\{l_1, l_2, \ldots, l_\nu\} \quad \text{and} \quad \mathbf{I}=\{i_1, i_2, \ldots, i_\nu\} \tag{4.24}$$

create excitations $|{}^{S,M}_{\zeta k_2}B^+_{\nu+\eta}\rangle$ with index sets

$$\tilde{\mathbf{L}}(\eta\zeta)=\{\tilde{l}_1, \tilde{l}_2, \ldots, \tilde{l}_{\nu+\eta}\}$$

and

$$\tilde{\mathbf{I}}(\eta\zeta)=\{\tilde{i}_1, \tilde{i}_2, \ldots, \tilde{i}_{\nu+\eta}\} \tag{4.25}$$

which differ from $\mathbf{L}$ and $\mathbf{I}$ by at most two elements. Ten special cases have to be distinguished depending on the form of the $(\nu+\eta)$-fold excitations $|{}^{S,M}_{\zeta k_2}B^+_{\nu+\eta}\rangle$. Denoting these excitations symbolically by $|\eta\zeta\rangle$

$$|01\rangle = |{}^{S,M}_{k_2}B^+_\nu\rangle \tag{4.26a}$$
$$|02\rangle = |{}^{S,M}_{k_2}B^+_\nu(m, l_\mu)\rangle \tag{4.26b}$$
$$|03\rangle = |{}^{S,M}_{k_2}B^+_\nu(j, i_\mu)\rangle \tag{4.26c}$$
$$|04\rangle = |{}^{S,M}_{k_2}B^+_\nu((l, l_\mu), (i, i_\lambda))\rangle \tag{4.26d}$$
$$|05\rangle = |{}^{S,M}_{k_2}B^+_\nu((l, l_\mu), (n, l_\lambda))\rangle \tag{4.26e}$$
$$|06\rangle = |{}^{S,M}_{k_2}B^+_\nu((i, i_\mu), (g, i_\lambda))\rangle \tag{4.26f}$$
$$|11\rangle = |{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(li)\rangle \tag{4.27a}$$
$$|12\rangle = |{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(li, (m, l_\mu))\rangle \tag{4.27b}$$
$$|13\rangle = |{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(li, (j, i_\mu))\rangle \tag{4.27c}$$
$$|21\rangle = |{}^{S,M}_{\tilde{k}_2}B^+_{\nu+2}(limj)\rangle \tag{4.28}$$

we obtain the following relationships between $\tilde{\mathbf{L}}(\eta\zeta)$ and $\tilde{\mathbf{I}}(\eta\zeta)$ (4.25), $\mathbf{L}$ and $\mathbf{I}$ [defined by (4.24)] and the summation variables g, i, j, l, m, n of (4.11)

$$\tilde{\mathbf{L}}(01)=\mathbf{L} \quad \text{and} \quad \tilde{\mathbf{I}}(01)=\mathbf{I} \tag{4.29a}$$
$$\tilde{\mathbf{L}}(02)=(\mathbf{L}-\{l_\mu\})\cup\{m\} \quad \text{and} \quad \tilde{\mathbf{I}}(02)=\mathbf{I} \tag{4.29b}$$
$$\tilde{\mathbf{L}}(03)=\mathbf{L} \quad \text{and} \quad \tilde{\mathbf{I}}(03)=(\mathbf{I}-\{i_\mu\})\cup\{j\} \tag{4.29c}$$
$$\tilde{\mathbf{L}}(04)=(\mathbf{L}-\{l_\mu\})\cup\{l\} \quad \text{and} \quad \tilde{\mathbf{I}}(04)=(\mathbf{I}-\{i_\mu\})\cup\{i\} \tag{4.29d}$$
$$\tilde{\mathbf{L}}(05)=(\mathbf{L}-\{l_\mu, l_\lambda\})\cup\{n, l\} \quad \text{and} \quad \tilde{\mathbf{I}}(05)=\mathbf{I} \tag{4.29e}$$
$$\tilde{\mathbf{L}}(06)=\mathbf{L} \quad \text{and} \quad \tilde{\mathbf{I}}(06)=(\mathbf{I}-\{i_\mu, i_\lambda\})\cup\{g, i\} \tag{4.29f}$$
$$\tilde{\mathbf{L}}(11)=\mathbf{L}\cup\{l\} \quad \text{and} \quad \tilde{\mathbf{I}}(11)=\mathbf{I}\cup\{i\} \tag{4.30a}$$
$$\tilde{\mathbf{L}}(12)=(\mathbf{L}-\{l_\mu\})\cup\{l, m\} \quad \text{and} \quad \tilde{\mathbf{I}}(12)=\mathbf{I}\cup\{i\} \tag{4.30b}$$
$$\tilde{\mathbf{L}}(13)=\mathbf{L}\cup\{l\} \quad \text{and} \quad \tilde{\mathbf{I}}(13)=(\mathbf{I}-\{i_\mu\})\cup\{i, j\} \tag{4.30c}$$
$$\tilde{\mathbf{L}}(21)=\mathbf{L}\cup\{l, m\} \quad \text{and} \quad \tilde{\mathbf{I}}(21)=\mathbf{I}\cup\{i, j\} \tag{4.31}$$

According to condition (4.19) only those terms in the matrix element expansion do not vanish for which the index sets $\tilde{\mathbf{L}}(\eta\zeta)$ and $\tilde{\mathbf{I}}(\eta\zeta)$ are equal to the index sets corresponding to the $(\nu+\eta)$-fold excitation $\langle{}^{S,M}_{k_1}B^+_{\nu+\eta}|$ in Eq. (4.6a)

$$\mathbf{M}=\{m_1, m_2, \ldots, m_{\nu+\eta}\} \quad \text{and} \quad \mathbf{J}=\{j_1, j_2, \ldots, j_{\nu+\eta}\}, \tag{4.32}$$

i.e., we have

$$\mathbf{M}=\tilde{\mathbf{L}}(\eta\zeta) \quad \text{and} \quad \mathbf{J}=\tilde{\mathbf{I}}(\eta\zeta). \tag{4.33}$$

The consequences of condition (4.33) are twofold [cf. (4.29)–(4.31)]:

For a matrix element between a $(\nu+\eta)$-fold and a ν-fold excitation to be nonvanishing one of the following ten conditions between the index sets $\{\mathbf{M}, \mathbf{J}\}$ and $\{\mathbf{L}, \mathbf{I}\}$ must apply:

For $\eta=0$ one of the following must hold

$$\mathbf{L}=\mathbf{M} \quad \text{and} \quad \mathbf{I}=\mathbf{J}, \tag{4.34a}$$
$$\mathbf{L}-(\mathbf{L}\cap\mathbf{M})=\{l_{\mu_1}\} \quad \text{and} \quad \mathbf{I}=\mathbf{J}, \tag{4.34b}$$
$$\mathbf{L}=\mathbf{M} \quad \text{and} \quad \mathbf{I}-(\mathbf{I}\cap\mathbf{J})=\{i_{\lambda_1}\}, \tag{4.34c}$$
$$\mathbf{L}-(\mathbf{L}\cap\mathbf{M})=\{l_{\mu_1}\} \quad \text{and} \quad \mathbf{I}-(\mathbf{I}\cap\mathbf{J})=\{i_{\lambda_1}\}, \tag{4.34d}$$
$$\mathbf{L}-(\mathbf{L}\cap\mathbf{M})=\{l_{\mu_1}, l_{\mu_2}\} \quad \text{and} \quad \mathbf{I}=\mathbf{J}, \tag{4.34e}$$
$$\mathbf{L}=\mathbf{M} \quad \text{and} \quad \mathbf{I}-(\mathbf{I}\cap\mathbf{J})=\{i_{\lambda_1}, i_{\lambda_2}\}. \tag{4.34f}$$

For $\eta=1$ one of the following must hold

$$\mathbf{L}\subset\mathbf{M} \quad \text{and} \quad \mathbf{I}\subset\mathbf{J}, \tag{4.35a}$$

$$\mathbf{L}-(\mathbf{L}\cap\mathbf{M})=\{l_{\mu_1}\} \quad \text{and} \quad \mathbf{I}\subset\mathbf{J}, \tag{4.35b}$$

$$\mathbf{L}\subset\mathbf{M} \quad \text{and} \quad \mathbf{I}-(\mathbf{I}\cap\mathbf{J})=\{i_{\lambda_1}\}, \tag{4.35c}$$

and for $\eta=2$ must hold

$$\mathbf{L}\subset\mathbf{M} \quad \text{and} \quad \mathbf{I}\subset\mathbf{J}. \tag{4.36}$$

In (4.34) and (4.35) we have denoted by l_{μ_1} and l_{μ_2} those orbital indices l_μ which are elements of the particle index set $\mathbf{L}$ but not of the set $\mathbf{M}$. The corresponding hole indices i_λ are denoted by i_{λ_1} and i_{λ_2}. Similarly we will denote by m_{ρ_1} and m_{ρ_2} those orbital indices which are in $\mathbf{M}$ but not in $\mathbf{L}$ and the corresponding hole indices of $\mathbf{J}$ by j_{σ_1} and j_{σ_2}.

(ii) From (4.33) can also be derived conditions satisfied by the summation variables g, i, j, l, m, n of (4.11) which give a contribution to a nonvanishing matrix element. The corresponding set of summation variables depends on the conditions (4.34)–(4.36). *Each condition yields a different matrix element formula.* We will state now the resulting ten final matrix element formulas which can be derived by simple set theoretical arguments and an analysis of the summations over the occupied and unoccupied orbitals in (4.11). Special care has to be taken to account for the possibility that the orbital indices of $\{\mathbf{M},\mathbf{J}\}$ and $\{\mathbf{L},\mathbf{I}\}$ may assume the same value twice in these sets. As an illustration for the logical arguments involved we provide in Appendix III the proof for the matrix element formula corresponding to condition (4.34e). The proofs of the remaining formulas[30] are similar, but rather lengthy, and, therefore, have been omitted here.

In the following matrix element formulas the function $\xi(r_1,r_2)$ and the summation index sets $[\mu_1]$ and $[\lambda_1]$ are introduced to distinguish single from double occupancies in the orbital index sets $\{\mathbf{L},\mathbf{I}\}$ and $\{\mathbf{M},\mathbf{J}\}$. They are defined by

$$\xi(r_1,r_2)=\begin{cases}\frac{1}{2} & \text{if} \quad r_1=r_2\\ 1 & \text{if} \quad r_1\neq r_2\end{cases} \tag{4.37}$$

and

$$[\mu_1]=\{\mu\in\{1,\ldots,\nu\}\,|\,l_\mu=l_{\mu_1} \text{ and } l_\mu,l_{\mu_1}\in\mathbf{L}\} \tag{4.38a}$$

$$[\lambda_1]=\{\lambda\in\{1,\ldots,\nu\}\,|\,i_\lambda=i_{\lambda_1} \text{ and } i_\lambda,i_{\lambda_1}\in\mathbf{I}\}. \tag{4.38b}$$

Formulas for the matrix elements between ν-fold excitations ($\eta=0$):

If $\mathbf{L}=\mathbf{M}$ and $\mathbf{I}=\mathbf{J}$: $\langle {}^{S,M}_{k_1}B^+_\nu|\hat H|{}^{S,M}_{k_2}B^+_\nu\rangle$

$$\begin{aligned}
&=\Big\{E_0+\sum_{\mu=1}^{\nu}[F_{l_\mu l_\mu}-F_{i_\mu i_\mu}]-\sum_{\mu,\lambda=1}^{\nu}(l_\mu l_\mu|i_\lambda i_\lambda)+\sum_{\mu<\lambda}[\xi(l_\mu,l_\lambda)(l_\mu l_\mu|l_\lambda l_\lambda)+\xi(i_\mu,i_\lambda)(i_\mu i_\mu|i_\lambda i_\lambda)]\Big\}\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu\rangle\\
&+\sum_{\mu<\lambda}\{\xi(l_\mu,l_\lambda)(l_\mu l_\lambda|l_\mu l_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((l_\mu,l_\lambda),(l_\lambda,l_\mu))\rangle+\xi(i_\mu,i_\lambda)(i_\mu i_\lambda|i_\mu i_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((i_\mu,i_\lambda),(i_\lambda,i_\mu))\rangle\}\\
&+\sum_{\mu,\lambda=1}^{\nu}2(l_\mu i_\lambda|l_\mu i_\lambda)\sum_{k_0=1}^{f^{2\nu}_{ST}}\sum_{\pi_{k'}\in T(k_0)}K^{S2\nu}_{k_0k_2}(\pi_k,\mu,\pi_{k'},\lambda)\ \langle {}^{S,M}_{k_1}B^+_\nu|\overline{(\pi_{k'}\mu,\pi_{k'}\lambda)}^{r-1}\,{}^{S,M}_{k_0}B^+_\nu\rangle .
\end{aligned} \tag{4.39a}$$

If condition (4.34b) holds then $\mathbf{M}-(\mathbf{M}\cap\mathbf{L})=\{m_{\rho_1}\}$ and

$$\begin{aligned}
\langle {}^{S,M}_{k_1}B^+_\nu|\hat H|{}^{S,M}_{k_2}B^+_\nu\rangle&=\sum_{\mu\in[\mu_1]}\Big[F_{m_{\rho_1}l_{\mu_1}}+\sum_{\substack{\lambda=1\\ \lambda\neq\mu}}^{\nu}\xi(l_\lambda,l_{\mu_1})\xi(l_\lambda,m_{\rho_1})(m_{\rho_1}l_{\mu_1}|l_\lambda l_\lambda)\Big]\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu(m_{\rho_1},l_\mu)\rangle\\
&+\sum_{\mu\in[\mu_1]}\sum_{\substack{\lambda=1\\ \lambda\neq\mu}}^{\nu}\xi(l_\lambda,l_{\mu_1})\xi(l_\lambda,m_{\rho_1})(l_\lambda l_{\mu_1}|m_{\rho_1}l_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((l_\lambda,l_\mu),(m_{\rho_1},l_\lambda))\rangle\\
&+\sum_{\mu\in[\mu_1]}\sum_{\lambda=1}^{\nu}\Big\{2(m_{\rho_1}i_\lambda|l_{\mu_1}i_\lambda)\sum_{k_0=1}^{f^{2\nu}_{ST}}\sum_{\pi_{k'}\in T(k_0)}K^{S2\nu}_{k_0k_2}(\pi_{k'}\mu,\pi_{k'}\lambda)\\
&\times\langle {}^{S,M}_{k_1}B^+_\nu|\overline{(\pi_{k'}\mu,\pi_{k'}\lambda)}^{r-1}\,{}^{S,M}_{k_0}B^+_\nu(m_{\rho_1},l_\mu)\rangle-(m_{\rho_1}l_{\mu_1}|i_\lambda i_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu(m_{\rho_1},l_\mu)\rangle\Big\}.
\end{aligned} \tag{4.39b}$$

If condition (4.34c) holds then $\mathbf{J}-(\mathbf{J}\cap\mathbf{L})=\{j_{\sigma_1}\}$ and

$$\langle {}^{S,M}_{k_1}B^+_\nu|\hat H|{}^{S,M}_{k_2}B^+_\nu\rangle=\sum_{\lambda\in[\lambda_1]}\Big[-F_{j_{\sigma_1}i_{\lambda_1}}+\sum_{\substack{\mu=1\\ \mu\neq\lambda}}^{\nu}\xi(i_\mu,i_{\lambda_1})\xi(i_\mu,j_{\sigma_1})(j_{\sigma_1}i_{\lambda_1}|i_\mu i_\mu)\Big]\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu(j_{\sigma_1},i_\lambda)\rangle$$

$$+\sum_{\lambda\in[\lambda_1]}\sum_{\substack{\mu=1\\ \mu\neq\lambda}}^{\nu}\xi(i_\mu,i_{\lambda_1})\xi(i_\mu,j_{\sigma_1})(i_\mu i_{\lambda_1}|j_{\sigma_1}i_\mu)\langle {}^{S,M}_{k_1}B^+_\nu|\,{}^{S,M}_{k_2}B^+_\nu((i_\mu,i_\lambda),(j_{\sigma_1},i_\mu))\rangle$$

$$+\sum_{\lambda\in[\lambda_1]}\sum_{\mu=1}^{\nu}\Bigg\{2(j_{\sigma_1}l_\mu|i_{\lambda_1}l_\mu)\sum_{k_0=1}^{f_{ST}^{2\nu}}\sum_{\pi_{k'}\in T(k_0)}K^{S2\nu}_{k_0k_2}(\pi_{k'}\mu,\pi_{k'}\lambda)$$

$$\times\langle {}^{S,M}_{k_1}B^+_\nu|\overline{(\pi_{k'}\mu,\pi_{k'}\lambda)}^{\nu-1}\,{}^{S,M}_{k_0}B^+_\nu(j_{\sigma_1},i_\lambda)\rangle-(j_{\sigma_1}i_{\lambda_1}|l_\mu l_\mu)\langle {}^{S,M}_{k_1}B^+_\nu|\,{}^{S,M}_{k_2}B^+_\nu(j_{\sigma_1},i_\lambda)\rangle\Bigg\}\,. \tag{4.39c}$$

If condition (4.34d) holds

$$\langle {}^{S,M}_{k_1}B^+_\nu|\hat H|\,{}^{S,M}_{k_2}B^+_\nu\rangle=2(m_{\rho_1}j_{\sigma_1}|l_{\mu_1}i_{\lambda_1})\sum_{\mu\in[\mu_1]}\sum_{\lambda\in[\lambda_1]}\sum_{k_0=1}^{f_{ST}^{2\nu}}\sum_{\pi_{k'}\in T(k_0)}K^{S2\nu}_{k_0k_2}(\pi_{k'}\mu,\pi_{k'}\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|\overline{(\pi_{k'}\mu,\pi_{k'}\lambda)}^{\nu-1}$$

$$\times\,{}^{S,M}_{k_0}B^+_\nu((m_{\rho_1},l_\mu),(j_{\sigma_1},i_\lambda))\rangle-(m_{\rho_1}l_{\mu_1}|j_{\sigma_1}i_{\lambda_1})\sum_{\mu\in[\mu_1]}\sum_{\lambda\in[\lambda_1]}\langle {}^{S,M}_{k_1}B^+_\nu|\,{}^{S,M}_{k_2}B^+_\nu((m_{\rho_1},l_\mu),(j_{\sigma_1},i_\lambda))\rangle\,. \tag{4.39d}$$

If condition (4.34e) holds then $\mathbf{M}-(\mathbf{M}\cap\mathbf{L})=\{m_{\rho_1},m_{\rho_2}\}$ and

$$\langle {}^{S,M}_{k_1}B^+_\nu|\hat H|\,{}^{S,M}_{k_2}B^+_\nu\rangle=\xi(m_{\rho_1},m_{\rho_2})\xi(l_{\mu_1},l_{\mu_2})\Bigg\{(m_{\rho_1}l_{\mu_1}|m_{\rho_2}l_{\mu_2})\sum_{\mu\in[\mu_1]}\sum_{\substack{\lambda\in[\mu_2]\\ \lambda\neq\mu}}\langle {}^{S,M}_{k_1}B^+_\nu|\,{}^{S,M}_{k_2}B^+_\nu((m_{\rho_1},l_\mu),(m_{\rho_2},l_\lambda))\rangle$$

$$+(m_{\rho_2}l_{\mu_1}|m_{\rho_1}l_{\mu_2})\sum_{\mu\in[\mu_1]}\sum_{\substack{\lambda\in[\mu_2]\\ \lambda\neq\mu}}\langle {}^{S,M}_{k_1}B^+_\nu|\,{}^{S,M}_{k_2}B^+_\nu((m_{\rho_2},l_\mu),(m_{\rho_1},l_\lambda))\rangle\Bigg\}\,. \tag{4.39e}$$

If condition (4.34f) holds then $\mathbf{J}-(\mathbf{J}\cap\mathbf{I})=\{j_{\sigma_1},j_{\sigma_2}\}$ and

$$\langle {}^{S,M}_{k_1}B^+_\nu|\hat H|\,{}^{S,M}_{k_2}B^+_\nu\rangle=\xi(j_{\sigma_1},j_{\sigma_2})\xi(i_{\lambda_1},i_{\lambda_2})\Bigg\{(j_{\sigma_1}i_{\lambda_1}|j_{\sigma_2}i_{\lambda_2})\sum_{\mu\in[\lambda_1]}\sum_{\substack{\lambda\in[\lambda_2]\\ \lambda\neq\mu}}\langle {}^{S,M}_{k_1}B^+_\nu|\,{}^{S,M}_{k_2}B^+_\nu((j_{\sigma_1},i_\mu),(j_{\sigma_2},i_\lambda))\rangle$$

$$+(j_{\sigma_2}i_{\lambda_1}|j_{\sigma_1}i_{\lambda_2})\sum_{\mu\in[\lambda_1]}\sum_{\substack{\lambda\in[\lambda_2]\\ \lambda\neq\mu}}\langle {}^{S,M}_{k_1}B^+_\nu|\,{}^{S,M}_{k_2}B^+_\nu((j_{\sigma_2},i_\mu),(j_{\sigma_1},i_\lambda))\rangle\Bigg\}\,. \tag{4.39f}$$

Formulas for the matrix elements between $(\nu+1)$- and ν-fold excitations ($\eta=1$):
If condition (4.35a) holds then $\mathbf{M}-\mathbf{L}=\{m_{\rho_1}\}$ and $\mathbf{J}-\mathbf{I}=\{j_{\sigma_1}\}$ and

$$\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\hat H|\,{}^{S,M}_{k_2}B^+_\nu\rangle=\sqrt{2}\Bigg(\Bigg\{F_{m_{\rho_1}j_{\sigma_1}}+\sum_{\mu=1}^{\nu}[\xi(m_{\rho_1},l_\mu)(m_{\rho_1}j_{\sigma_1}|l_\mu l_\mu)-\xi(j_{\sigma_1},i_\mu)(m_{\rho_1}j_{\sigma_1}|i_\mu i_\mu)]\Bigg\}$$

$$\times\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(m_{\rho_1}j_{\sigma_1})\rangle+\sum_{\mu=1}^{\nu}\{\xi(m_{\rho_1},l_\mu)(l_\mu j_{\sigma_1}|m_{\rho_1}l_\mu)\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(l_\mu j_{\sigma_1},(m_{\rho_1},l_\mu))\rangle$$

$$-\xi(j_{\sigma_1},i_\mu)(i_\mu j_{\sigma_1}|m_{\rho_1}i_\mu)\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(m_{\rho_1}i_\mu,(j_{\sigma_1},i_\mu))\rangle\}\Bigg)\,. \tag{4.40a}$$

If condition (4.35b) holds then $\mathbf{M}-\mathbf{L}=\{m_{\rho_1},m_{\rho_2}\}$ and

$$\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\hat H|\,{}^{S,M}_{k_2}B^+_\nu\rangle=\sqrt{2}\,\xi(m_{\rho_1},m_{\rho_2})\Bigg\{(m_{\rho_1}j_{\sigma_1}|m_{\rho_2}l_{\mu_1})\sum_{\mu\in[\mu_1]}\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(m_{\rho_1}j_{\sigma_1},(m_{\rho_2},l_\mu))\rangle$$

$$+(m_{\rho_2}j_{\sigma_1}|m_{\rho_1}l_{\mu_1})\sum_{\mu\in[\mu_1]}\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(m_{\rho_2}j_{\sigma_1},(m_{\rho_1},l_\mu))\rangle\Bigg\}\,. \tag{4.40b}$$

If condition (4.35c) holds then $\mathbf{J}-\mathbf{I}=\{j_{\sigma_1},j_{\sigma_2}\}$ and

$$\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\hat H|\,{}^{S,M}_{k_2}B^+_\nu\rangle=-\sqrt{2}\,\xi(j_{\sigma_1},j_{\sigma_2})\Bigg\{(m_{\rho_1}j_{\sigma_1}|j_{\sigma_2}i_{\lambda_1})\sum_{\lambda\in[\lambda_1]}\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(m_{\rho_1}j_{\sigma_1},(j_{\sigma_2},i_\lambda))\rangle$$

$$+(m_{\rho_1}j_{\sigma_2}|j_{\sigma_1}i_{\lambda_1})\sum_{\lambda\in[\lambda_1]}\langle {}^{S,M}_{k_1}B^+_{\nu+1}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+1}(m_{\rho_1}j_{\sigma_2},(j_{\sigma_1},i_\lambda))\rangle\Bigg\}\,. \tag{4.40c}$$

Formula for the matrix elements between $(\nu+2)$- and ν-fold excitations ($\eta=2$):
If condition (4.36) holds then $\mathbf{M}-\mathbf{L}=\{m_{\rho_1},m_{\rho_2}\}$ and $\mathbf{J}-\mathbf{I}=\{j_{\sigma_1},j_{\sigma_2}\}$ and we have

$$\langle {}^{S,M}_{k_1}B^+_{\nu+2}|\hat H|\,{}^{S,M}_{k_2}B^+_\nu\rangle=2\xi(m_{\rho_1},m_{\rho_2})\xi(j_{\sigma_1},j_{\sigma_2})\{(m_{\rho_1}j_{\sigma_1}|m_{\rho_2}j_{\sigma_2})\langle {}^{S,M}_{k_1}B^+_{\nu+2}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+2}(m_{\rho_1}j_{\sigma_1}m_{\rho_2}j_{\sigma_2})\rangle$$

$$+(m_{\rho_1}j_{\sigma_2}|m_{\rho_2}j_{\sigma_1})\langle {}^{S,M}_{k_1}B^+_{\nu+2}|\,{}^{S,M}_{\tilde{k}_2}B^+_{\nu+2}(m_{\rho_1}j_{\sigma_2}m_{\rho_2}j_{\sigma_1})\rangle\}\,. \tag{4.41}$$

V. DISCUSSION OF THE MATRIX ELEMENT FORMULAS

The general matrix element formulas (4.39)–(4.41) for ν-fold irreducible products ${}^{S,M}_{k}B^{+}_{\nu}$ of single excitations completely describe all nonvanishing matrix elements (4.6a) of the Hamiltonian in the SAAP basis. One can assume that the AIP ${}^{S,M}_{k}B^{+}_{\nu}$ is one of the $f^{2\nu}_{ST}$ [cf. (A1.23)] t-type representatives (3.36a) since every SAAP creation operator (3.11) may be expressed through the latter if the proper normalization constant (3.14a) and the proper t-type preserving permutation (3.36b) of the orbital configuration have been chosen.

The matrix elements are represented as weighted sums of one- and two-electron integrals. The set of such integrals which enters a particular matrix element is determined by the two orbital sets $\{\mathbf{M},\mathbf{J}\}$ and $\{\mathbf{L},\mathbf{I}\}$ of the $(\nu+\eta)$- and ν-fold excitations defining the matrix element. The larger the difference sets $\mathbf{M}-\mathbf{L}$ and $\mathbf{J}-\mathbf{I}$ are, the smaller is this set of spatial integrals.

The expressions in the general formulas from which the weights C in (1.1) can be determined, in addition to the orbital sets $\{\mathbf{M},\mathbf{J}\}$ and $\{\mathbf{L},\mathbf{I}\}$, depend on the order of the particles and holes in the orbital configurations $(\mathbf{M},\mathbf{J})$ and $(\mathbf{L},\mathbf{I})$ and on the Serber genealogies k_1 and k_2 (A1.2c) of the spin coupling. Beside the trivial factors $\xi(r_1,r_2)$ [cf. Eq. (4.37)] accounting for double occupancies the weights entail two contributions.

A first contribution is due to the coefficients $K^{S2\nu}_{k_0k_2}(\pi_{k'}\mu,\pi_{k'}\lambda)$ [cf. Eq. (4.15a)] which appear in the formulas for matrix elements of ν-fold excitations (4.39a)–(4.39d). These coefficients depend only on the genealogy k_2 and can be conceived as ν-dimensional matrices $(\mu,\lambda=1,\ldots,\nu)$. Because of (4.15b) there are only $f^{2(\nu-1)}_{S}f^{2\nu}_{ST}$ nonvanishing matrices of this kind which are determined by the ν^2 Serber matrices representing the permutations $(\pi_{k'}\mu,\pi_{k'}\lambda)$ of $S^{\nu}\times S^{\nu}$. A calculation of the coefficient matrices, a prerequisite for a computer program based on the formulas given above, has shown that they are very sparse. For instance, for $\nu=4$ and $S=0$ only 151 of the 480 coefficients do not vanish and assume only 21 different values. These values can easily be taken over as constants into the source code of a CI program. As a result in (4.39a)–(4.39d) the double sum over k_0 and $\pi_{k'}$ reduces from $f^{8}_{0}=14$ to one or two terms for nearly all pairs (μ,λ).

A second most important contribution to the weights stems from the various scalar products of the $(\nu+\eta)$-fold excitation $\langle {}^{S,M}_{k_1}B^{+}_{\nu+\eta}|$ with the $(\nu+\eta)$-fold excitations $|\eta\xi\rangle$ [cf. Eq. (4.26)] created by the Hamiltonian from $|{}^{S,M}_{k_2}B^{+}_{\nu}\rangle$. Since the orbital configurations of these $(\nu+\eta)$-fold excitations have to be identical [cf. Eq. (4.33)], their scalar product is given by (4.22) as a sum of Serber matrix elements. These Serber matrices serve as the parameter list for the weight generation. If up to ν-fold excitations are included in a CI expansion the length N_g of this parameter list is given by

$$N_g=\tfrac{1}{4}f^{2\nu}_{ST}(f^{2\nu}_{ST}+1)\nu!(\nu!+1)\ . \tag{5.1}$$

(5.1) follows from the even–odd symmetry (4.23) of the Serber matrices of $S^{\nu}\times S^{\nu}$ and from the fact that only the submatrices corresponding to t-type representatives have to be considered. Table I gives N_g for various ν and S to demonstrate that for configurations not higher than quadruply excited the parameters are few enough to be stored in the central memory of a computer. [The parameter list for the ν-fold excitations contains, of course, that for the $(\nu-1)$-fold excitations since the Serber representation is adapted to the chain of subgroups $S^{2\nu}\supset S^{2(\nu-1)}\ldots$ (cf. Appendix I)].

One can reduce the length of the parameter list for the scalar product calculation taking recourse to the representation matrices of S^{ν} rather than those of $S^{\nu}\times S^{\nu}$. This reduction is based on the relation between the representation matrices of the permutations (p_m,p_j) of $S^{\nu}\times S^{\nu}$ and those of the permutations (p_m,e) and (p_j^{-1},e) of S^{ν}

$$U^{S2\nu}_{kk'}(p_m,p_j)=\alpha_0(k')\sum_{l=1}^{f^{2\nu}_{S}}\alpha_0(l)U^{S2\nu}_{kl}(p_m,e)U^{S2\nu}_{k'l}(p_j^{-1},e)\ . \tag{5.2}$$

The appearance of the parities $\alpha_0(k)$ indicates that the even–odd symmetry (A1.30) has been used for the derivation of (5.2). The length N_{gr} of the new parameter list is given by

$$N_{gr}=\nu!\,f^{2\nu}_{ST}f^{2\nu}_{S}\ . \tag{5.3}$$

The pertinent values of N_{gr} are given in Table II.

Since the Serber matrices of $S^{\nu}\times S^{\nu}$ and of S^{ν} are relatively sparse one might reduce even further the size of the parameter lists by storing only the nonvanishing elements. However, any such reduction is accompanied by an increase of computational work [cf. (5.2)] and, consequently, makes the algorithm for the matrix element generation less efficient.

For our CI studies on the excited states of polyenes[28] and polyacenes[29] the inclusion of at most quadruple excitations into the CI expansion appeared to be sufficient. The corresponding computer program used the more ef-

TABLE I. Values of N_g.

ν \ S	0	1	2	3
2	9	9		
3	126	315	126	
4	6 300	19 800	13 500	3 000
5	566 280	2 548 860	2 178 000	762 300

TABLE II. Values of N_{gr}.

ν \ S	0	1	2	3
2	8	12		
3	90	270	90	
4	2 016	7 392	4 320	672
5	60 480	280 800	216 000	588 000

ficient algorithm with the Serber matrices of $S^\nu \times S^\nu$ as parameters.

The Serber matrix elements necessary for the calculation of the scalar products can be selected very efficiently. The permutations (p_m, p_j) corresponding to the configurations $[\mathrm{L}(\eta\zeta), \mathrm{I}(\eta\zeta)]$ can be obtained in an efficient way by coding the orbital configuration $(\mathbf{M}, \mathbf{J})$ of the excitation $\langle {}^{S,M}_{kl}B^{\dagger}_{\nu+\eta}|$ into an array of length $N_h + N_p$. Addition of the $2^{M_p+M_h}$ parameters selected [see Eq. (4.22)] completes the scalar product calculation. For $\nu = 4$ and $S = 1$, for instance, in the worst case eight and in the best case no additions have to be performed.

Consequently the determination of the weights C in the formulas (1.1) in our method amounts to only a few additions followed by a few multiplications by the factors discussed above. In the CI method of Segal *et al.*,[22] for comparison, scalar products of two $f_S^{2\nu}$ dimensional parameter vectors have to be formed for the calculation of a weight C^{ab}_{ijkl} of a general two-particle integral. In the case $\nu = 4$ and $S = 1$, for instance, 28 multiplications and additions have to be carried out for the generation of a weight factor. In view of this, our method for the generation of CI matrices appears to be a promising alternative to the unitary group approach.

ACKNOWLEDGMENTS

The authors like to thank W. A. Bingel for useful suggestions. We are grateful to A. Weller for his continuous support. P. T. has benefited much from a stimulating summer school organized by the quantum chemistry group of Upsala University. This work has been supported in part by a grant of the Kultusministerium des Landes Niedersachsen for a Jerusalem–Göttingen exchange program. The use of the excellent computer facilities of the Gesellschaft für wissenschaftliche Datenverarbeitung Göttingen and friendly help by its staff is also acknowledged.

APPENDIX I: SPIN FUNCTIONS AND ORTHOGONAL REPRESENTATIONS OF THE SYMMETRIC GROUP S^N

Let $\Theta^N_{S,M,k}$ designate state vectors of total spin (S, M) formed from N identical spins $\frac{1}{2}$. These vectors span an irreducible representation of S^N. The representation can be labeled by a Young diagram $[\frac{1}{2}N+S, \frac{1}{2}N-S]$ corresponding to a partition of the integer N. (A Young diagram $[l_1, l_2, \ldots, l_m]$ corresponds to the partition

$$l_1 + l_2 + \cdots + l_m = N\,, \qquad l_1 \geq l_2 \geq \cdots \geq l_m\,,$$

and entails l_1 boxes in the first row, l_2 boxes in the second row etc.)

A. Yamanouchi-Kotani (YK) spin functions

A widespread construction of orthonormal spin functions is the "genealogical" construction of Yamanouchi[52] and Kotani *et al.*[53] which couples to a first electron spin $\sigma \in \{\alpha, \beta\}$ a second electron spin, and continues this way always coupling the spin of the qth electron to the total spin of the $q-1$ preceding electrons. The spin functions obtained are eigenfunctions of the $N-2$ intermediate spin operators

$$\hat{\mathbf{S}}^2_{1,q} = \left(\sum_{\mu=1}^{q} \hat{\sigma}_\mu\right)^2 \qquad q = 2, \ldots, N-1 \tag{A1.1a}$$

which commute with the total spin operator $\hat{\mathbf{S}}^2$ and the spin operator $\hat{\sigma}^2$ of the first electron. Such a system of $N-2$ intermediate spin operators is called a "coupling scheme." Every YK function is uniquely characterized by the "genealogy" of the spin quantum numbers $S_{1,q}$ of these operators, which can be combined to the genealogy symbol $\hat{k}$

$$\hat{k} = (S_{1,2}, S_{1,3}, S_{1,4}, \ldots, S_{1,N-1})\,. \tag{A1.1b}$$

There are f^N_S (1.16) different symbols $\hat{k}$ for a given pair (N, S). Therefore, every symbol $\hat{k}$ can be identified by a number $\hat{k} = 1, \ldots, f^N_S$, which then uniquely characterizes a YK function $\Theta^N_{S,M,\hat{k}}$.

B. Young's orthogonal representation

For the YK representation matrices of S^N follows from the coupling scheme (A1.1a) that the representations of the subgroups $S^{N-1}, S^{N-2}, \ldots, S^2$ are fully reduced, i.e., the YK representation is adapted to the sequence of subgroups $S^{N-1} \supset S^{N-2} \supset \cdots \supset S^2$.[55] Pauncz[56] has shown, that the YK representation is identical with Young's orthogonal representation.[54] The matrices of the latter can easily be determined from the "standard tableaux" which are constructed from the Young diagram $[\frac{1}{2}N+S, \frac{1}{2}N-S]$ (see for example Ref. 54). We call the YK–Young representation "standard representation" of S^N.[17]

C. Serber spin functions

For a system containing an even number of electrons the corresponding orbital configurations always contain an even number 2ν of singly occupied orbitals. Therefore orthonormal spin functions for 2ν spins $\frac{1}{2}$ have to be constructed. For this purpose it is advantageous (as will become clear below) to use the Serber[33] coupling scheme instead of the YK coupling scheme described above. The $2\nu-2$ spin operators of the *Serber coupling scheme* are the ν geminal spin operators

$$\hat{\mathbf{S}}^2_{q-1,q} = (\hat{\sigma}_{q-1} + \hat{\sigma}_q)^2 \qquad q = 2, 4, \ldots, 2\nu \tag{A1.2a}$$

and the $\nu-2$ intermediate operators

$$\hat{\mathbf{S}}^2_{1,q} = \left(\sum_{\mu=1}^{q} \hat{\sigma}_\mu\right)^2 \qquad q = 4, 6, \ldots, 2\nu-2\,. \tag{A1.2b}$$

Any Serber function is uniquely characterized by the genealogy symbol k of the corresponding spin quantum numbers

$$k = (S_{1,2}, S_{3,4}, S_{1,4}, S_{5,6}, S_{1,6}, \ldots, S_{2\nu-1,2\nu}) \tag{A1.2c}$$

which again can be identified by numbers $k = 1, \ldots, f^{2\nu}_S$. The geminal spin functions are given by $(q = 2, 4, \ldots, 2\nu)$

$$\theta_{0,0}(q-1, q) = \frac{1}{\sqrt{2}}[\alpha(q-1)\beta(q) - \beta(q-1)\alpha(q)] \tag{A1.3a}$$

$$\theta_{1,1}(q-1, q) = \alpha(q-1)\alpha(q) \tag{A1.3b}$$

$$\theta_{1,0}(q-1, q) = \frac{1}{\sqrt{2}}[\alpha(q-1)\beta(q) + \beta(q-1)\alpha(q)] \tag{A1.3c}$$

$$\theta_{1,-1}(q-1, q) = \beta(q-1)\beta(q) \tag{A1.3d}$$

The 2ν-electron Serber functions are constructed then by means of

$$\Theta^{q}_{S,M,k}=\sum_{M_q}(SM|S'M'-M_qS_{q-1,q}M_q)$$

$$\times\Theta^{q-2}_{S',M'-M_q,k'}\,\theta_{S_{q-1,q},M_q}\,. \qquad \text{(A1.4)}$$

The coefficients in (A1.4) are the Wigner[62] coefficients which guarantee the functions $\Theta^{q}_{S,M,k}$ to be orthonormal. The q-particle genealogy symbol k is obtained recursively from the $(q-2)$-particle symbol k' according to $k=(k',S',S_{q-1,q})$.

In every coupling step there are four possibilities to obtain the spin S of q electrons from the spin S' of $q-2$ electrons. These possibilities are illustrated in Fig. 2. In a Serber "branching diagram" presented in Fig. 3 every Serber function is characterized by a certain coupling route from the point $(0,0)$ to $(2\nu,S)$.

D. Serber representation

The Serber representation $S^{2\nu}$ is adapted to the sequence of subgroups $S^{2(\nu-1)}\supset S^{2(\nu-2)}\supset\cdots\supset S^2$ and to the geminal two-electron subgroups.

For the calculation of the representation matrices several possibilities exist. On the basis of group theoretical arguments Salmon[57] showed how one can determine Serber functions and matrices nonrecursively. Salmon *et al.*[58] presented an algorithm for the numerical computation of the Serber functions while Paldus and Wormer[59] derived formulas for the Serber representation matrices of the transpositions. One can obtain the Serber functions also by means of an orthogonal transformation from the YK functions $\Theta^{N}_{S,M,\hat{k}}$

$$\Theta^{N}_{S,M,k}=\sum_{\hat{k}}{}^{S,N}A_{\hat{k}k}\Theta^{N}_{S,M,\hat{k}} \qquad \text{(A1.5)}$$

and the Serber matrices by the corresponding similarity transformation from the Young matrices. This method allows to take advantage of the simple construction of the YK "standard" representation. Kaplan[17] derived the transformation matrices $A_{\hat{k}k}$ from Young diagrams. Horie[60] provided a recursive method for the construction of $A_{\hat{k}k}$ (see also Klein *et al.*[55] for a further group-theoretical derivation). Recently Wilson[61] developed a simple graphical method for the determination of the transformation matrices. In our calculations we have employed the Horie algorithm for the construction of the Serber matrices.

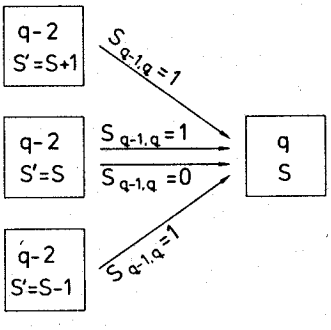

FIG. 2. Representation of the four coupling routes in the Serber scheme which lead from a spin S' for q-2 electrons to a spin S for q electrons.

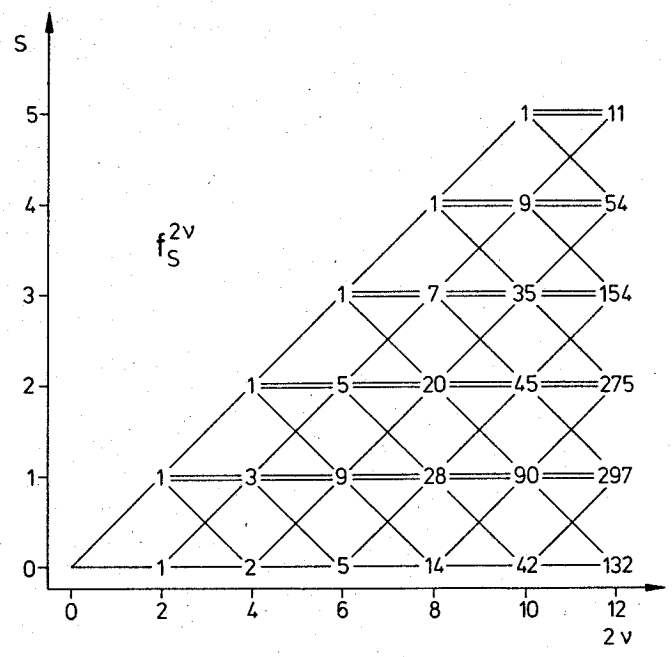

FIG. 3. Serber branching diagram: Every Serber function $\Theta^{2\nu}_{S,M,k}$ of the irreducible representation $[\nu+S,\ \nu-S]$ is characterized by a particular route k connecting the point $(0,0)$ in this diagram with the point $(2\nu,S)$. At each intersection $(2\nu,S)$ is given the number $f^{2\nu}_{S}$ of different routes from $(0,0)$ to $(2\nu,S)$.

We will now consider the properties of the Serber functions in more detail and define several distinguished subgroups of the symmetric group $S^{2\nu}$.

E. Algebraic structure of Serber functions and distinguished subgroups of $S^{2\nu}$

According to (A1.3) and (A1.4) the Serber functions are given by

$$\Theta^{2\nu}_{S,M,k}=\sum_{\sigma_1\cdots\sigma_{2\nu}}{}^{S,M}_{k}T_{\sigma_1\cdots\sigma_{2\nu}}\sigma_1\cdots\sigma_{2\nu}\,. \qquad \text{(A1.6)}$$

The 2ν-fold tensor products $\sigma_1\cdots\sigma_{2\nu}$ of one-particle spin functions σ in (A1.6) form an orthonormal basis in the 2ν-particle spin space. The matrix of coupling coefficients ${}^{S,M}_{k}T_{\sigma_1\cdots\sigma_{2\nu}}$ defines an orthogonal transformation in the 2ν-particle spin space. The orthogonality conditions for **T** read

$$\sum_{\sigma_1\cdots\sigma_{2\nu}}{}^{S,M}_{k}T_{\sigma_1\cdots\sigma_{2\nu}}\,{}^{S',M'}_{k'}T_{\sigma_1\cdots\sigma_{2\nu}}=\delta_{S,S'}\delta_{M,M'}\delta_{k,k'}\,. \qquad \text{(A1.7)}$$

T is called "reducing transformation" as it "reduces" the tensorial set of products $\sigma_1\cdots\sigma_{2\nu}$ to a tensorial set of eigenfunctions of $\hat{\mathbf{S}}^2$ (see Ref. 62 and Sec. III).

Let $\overline{P}^{\sigma}$ denote the unitary operator which affects the permutation $p^{-1}\in S^{2\nu}$ of the spin *functions* in the tensor product $\sigma_1\cdots\sigma_{2\nu}$

$$\overline{P}^{\sigma}\sigma_1\cdots\sigma_{2\nu}=\sigma_{p^{-1}(1)}\cdots\sigma_{p^{-1}(2\nu)}\,. \qquad \text{(A1.8)}$$

The operators $\overline{P}^{\sigma}$ span an operator representation $\overline{S}^{2\nu}$ of the permutation group $S^{2\nu}$. As is well known[17] the operators $\overline{P}^{\sigma}$ permuting the one particle *functions* act inversely to the permutation operators $\hat{P}^{\sigma}$ defined in Sec. I acting on the *coordinates*

$$\overline{P}^{\sigma}\sigma_1\cdots\sigma_{2\nu}(1,\ldots,2\nu) = (\hat{P}^{\sigma})^{-1}\sigma_1\cdots\sigma_{2\nu}(1,\ldots,2\nu)\ . \tag{A1.9}$$

Therefore, according to (1.20), the Serber representation for the operators $\overline{P}^{\sigma}$ is given by

$$\overline{P}^{\sigma}\Theta^{2\nu}_{S,M,k} = \sum_{l=1}^{f^{2\nu}_S} V^{S2\nu}_{lk}(p^{-1})\Theta^{2\nu}_{S,M,l} \tag{A1.10}$$

The fact that the Serber functions span a representation of $S^{2\nu}$ is due to the permutational symmetry of the reducing transformation **T** for which one obtains from (A1.10)

$$^{S,M}_{k}T_{\sigma_{p(1)}\cdots\sigma_{p(2\nu)}} = \sum_{l=1}^{f^{2\nu}_S} V^{S2\nu}_{lk}(p^{-1})\ {}^{S,M}_{l}T_{\sigma_1\cdots\sigma_{2\nu}}\ . \tag{A1.11}$$

Up to now the special geminal structure of the Serber coupling scheme has not yet been considered so that the above statements are valid for all types of orthonormal spin functions. In order to account for the geminal structure we express the Serber functions [equivalently to (A1.6)] as linear combinations of ν-fold tensor products of geminal spin functions (A1.3)

$$\Theta^{2\nu}_{S,M,k} = \sum_{M_1,\ldots,M_\nu} {}^{S,M}_{k}G_{M_1\cdots M_\nu}\theta_{S_1,M_1}\cdots\theta_{S_\nu,M_\nu}\ . \tag{A1.12}$$

The unitary operators $\overline{P}^{\theta}$, which cause a permutation $p^{-1} \in S^{\nu}$ of the spin geminals in the Serber function (A1.12), form an operator representation $\overline{S}^{\nu}$ of the subgroup $S^{\nu} \subset S^{2\nu}$ where the elements $p \in S^{\nu}$ are embedded into the group $S^{2\nu}$ as follows: Let $S^{\nu}_o(S^{\nu}_e)$ be the subgroup of $S^{2\nu}$ which permutes only the objects with odd (even) indices among the 2ν objects $a_1, a_2, \ldots, a_{2\nu}$. Then the neighbor transpositions of S^{ν}, from which all permutations can be created, are embedded into $S^{2\nu}$ according to ($\mu = 1, 2, \ldots, \nu-1$)

$$(\mu,\mu+1)\in S^{\nu} \rightarrow (2\mu-1,2\mu+1)\in S^{\nu}_o \subset S^{2\nu} \tag{A1.13a}$$

$$(\mu,\mu+1)\in S^{\nu} \rightarrow (2\mu,2\mu+2)\in S^{\nu}_e \subset S^{2\nu}\ . \tag{A1.13b}$$

Equation (A1.13) defines an isomorphism between the direct product $S^{\nu}\times S^{\nu}$ and the subgroup $S^{\nu}_o \times S^{\nu}_e$ of $S^{2\nu}$

$$(p,\tilde{p})\in S^{\nu}\times S^{\nu} \rightarrow p_o\tilde{p}_e \in S^{\nu}_o \times S^{\nu}_e \subset S^{2\nu}\ . \tag{A1.14a}$$

We will therefore identify the elements of these two groups from now on, i.e.,

$$(p,\tilde{p}) \equiv p_o\tilde{p}_e\ . \tag{A1.14b}$$

The "diagonal" elements (p,p) form a subgroup $[S^{\nu}\times S^{\nu}]_d$ of $S^{\nu}\times S^{\nu}$ which is isomorphic to S^{ν} such that we can identify also the elements of these two groups, i.e.,

$$(p,p) \equiv p\ . \tag{A1.15a}$$

Apparently (A1.15a) by virtue of (A1.14) and (A1.13) defines the embedding of S^{ν} into $S^{2\nu}$ which we wanted to construct. This yields the identity for the corresponding permutation operators

$$\overline{P}^{\theta} \equiv \overline{(P,P)}^{\sigma}\ . \tag{A1.15b}$$

Beside the subgroups $S^{\nu} \subset S^{\nu}\times S^{\nu} \subset S^{2\nu}$ defined above the Serber coupling scheme distinguishes the geminal subgroups S^2_{μ}, $\mu = 1, \ldots, \nu$, entailing the intrageminal transpositions $(2\mu-1, 2\mu) \in S^{2\nu}$.

Based on a further analysis of the Serber functions we will show now that the Serber matrices assume a particularly simple structure and exhibit useful symmetry properties for the subgroups mentioned above.

F. The "t-type" of the Serber functions

In order to investigate the properties of the representation matrices of the subgroup S^{ν} of spin geminal permutations we consider first the special way in which the singlet geminals (A1.3a) enter a Serber function.

According to (A1.4) the singlet geminals appear in a Serber function simply as *scalar factors*. The number of such singlet spin geminals in a Serber function $\Theta^{2\nu}_{S,M,k}$ for given ν and S depends only on k. We denote this number by $n(k)$ which obeys

$$n(k) \le \nu - S\ . \tag{A1.16}$$

If $S>0$, $n(k)$ can assume all values between 0 and $\nu-S$. For $S=0$ holds the additional condition $n(k) \neq \nu-1$. The number of possible values for $n(k)$ is given by

$$\left|\{n(k)\,|\,\nu,S\}\right| = \min(\nu+1-S,\nu)\ . \tag{A1.17}$$

In the set of Serber functions

$$\mathbf{C}^{2\nu}_{S,M} = \{\Theta^{2\nu}_{S,M,k}\,|\,k=1,\ldots,f^{2\nu}_S\}\ , \tag{A1.18}$$

$n(k)$ defines an equivalence relation

$$\Theta^{2\nu}_{S,M,k} \overset{=}{n} \Theta^{2\nu}_{S,M,k'} \Leftrightarrow n(k) = n(k')\ . \tag{A1.19}$$

We say $\Theta^{2\nu}_{S,M,k}$ is in the class $\mathbf{C}^{2\nu}_{S,M}(n)$, if $n(k)=n$.

Now consider a given class $\mathbf{C}^{2\nu}_{S,M}(n)$ of Serber functions. Omitting the n singlet geminals in the functions of $\mathbf{C}^{2\nu}_{S,M}(n)$ one can construct a set of $2(\nu-n)$ particle functions. The new spin functions $\Theta^{2(\nu-n)}_{S,M,\underline{k}}$ are in the class $\mathbf{C}^{2(\nu-n)}_{S,M}(0)$, i.e., they contain only triplet spin geminals.

The class $\mathbf{C}^{2(\nu-n)}_{S,M}(0)$ contains $P'(\nu-n,S)$ elements, where

$$P'(\nu-n,S) = P(\nu-n,S) - P(\nu-n,S+3)\ . \tag{A1.20a}$$

Here $P(N,S)$ is defined by

$$P(N,S) = \sum_{\kappa=I(N,S)}^{\min(N-S,N-1)} \binom{N-1}{\kappa}\binom{\kappa}{2\kappa-(N-S)} \tag{A1.20b}$$

with

$$I(N,S) = \begin{cases} \frac{1}{2}(N-S) & \text{for } N-S \text{ even} \\ \frac{1}{2}(N+1-S) & \text{for } N-S \text{ odd} \end{cases}\ . \tag{A1.20c}$$

The distribution $P'(\nu-n,S)$ can be determined from the branching diagram in Fig. 4 as the number of different coupling routes from (0, 0) to $(\nu-n,S)$. Every element in $\mathbf{C}^{2(\nu-n)}_{S,M}(0)$ is characterized by a genealogy symbol $\underline{k}$ labeling the routes in Fig. 4. As the geminal spin functions are of triplet type, k is solely determined by the $\nu-n-2$ spin quantum numbers of the intermediate spin operators (A1.2b)

$$\underline{k} = (S_{1,4}, S_{1,6}, \ldots, S_{1,2(\nu-n)-2})\ . \tag{A1.21}$$

We call k the "triplet spin coupling type" or simply "t-type" of the Serber function from which it is derived.

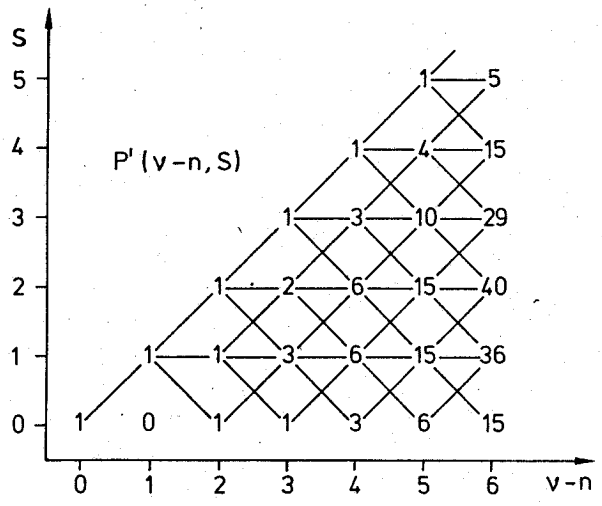

FIG. 4. Branching diagram representing the *triplet spin coupling routes* $\underline{k}$ of the Serber functions $\Theta^{2(\nu-n)}_{S,M,\underline{k}}$. At each intersection $(\nu-n, S)$ is given the number $P'(\nu-n, S)$ [cf. Eq. (A1.20)] of different triplet coupling routes $(0,0)$ to $(\nu-n, S)$. The singlet coupling steps in Figs. 2 and 3 are neither represented nor counted.

The t-types define the equivalence relation in the class $\mathbf{C}^{2\nu}_{S,M}(n)$

$$n(k)=n(k') \Rightarrow [\Theta^{2\nu}_{S,M,k}\,\underline{\bar{k}}\,\Theta^{2\nu}_{S,M,k'} \Longleftrightarrow \underline{k}=\underline{k}'] \,. \qquad \text{(A1.22)}$$

According to (A1.21) the relationships (A1.22) and (A1.19) can be summarized by the statement that the triplet spin coupling types $\underline{k}$ induce a disjoint decomposition of the set of Serber functions (A1.18) into equivalence classes. These classes will be denoted by $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$. Obviously each of these classes contains $\binom{\nu}{n}$ elements and every class $\mathbf{C}^{2\nu}_{S,M}(n)$ contains $P'(\nu-n, S)$ classes $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$. For given ν and S there are $f^{2\nu}_{ST}$ classes $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$

$$f^{2\nu}_{ST}=\sum_{n=0}^{\nu-S} P'(\nu-n, S) \,. \qquad \text{(A1.23)}$$

The dimension $f^{2\nu}_{S}$ of the representation $[\nu+S, \nu-S]$ is [cf. (1.16)]

$$f^{2\nu}_{S}=\sum_{n=0}^{\nu-S}\binom{\nu}{n} P'(\nu-n, S) \,. \qquad \text{(A1.24)}$$

The number $f^{2\nu}_{ST}$ of different triplet spin coupling types $\underline{k}$ is much smaller than the dimension of the representation if $2\nu>4$ and $S<\nu$. This is illustrated by a comparison of Figs. 3 and 5 the latter showing a branching diagram for $f^{2\nu}_{ST}$.

Definition: The Serber function $\Theta^{2\nu}_{S,M,k_0}$ of $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$

$$\Theta^{2\nu}_{S,M,k_0}=(\theta_{0,0})^n\,\Theta^{2(\nu-n)}_{S,M,\underline{k}} \qquad \text{(A1.25)}$$

is called the *representative* of the class $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$.

One can express every Serber function of t-type $\underline{k}$ by the representative of the corresponding class. This possibility is exploited in Sec. IV for an effective reduction of the dimension $f^{2\nu}_{S}$ of the representation $[\nu+S, \nu-S]$ to the number $f^{2\nu}_{ST}$ of different t-types.

G. "t-type" preserving permutations and their representation matrices

To each class $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$ corresponds a unique decomposition of the geminal permuting group $\bar{S}^{\nu}$. Let $\bar{S}^{n}$ be the subgroup permuting the singlet geminals $\theta^1_0 \cdots \theta^n_0$ in the representative (A1.25) of the class and $\bar{S}^{\nu-n}$ the subgroup permuting the triplet geminals $\theta^{n+1}_1 \cdots \theta^{\nu}_1$. Let furthermore $\bar{T}(k_0)\subset\bar{S}^{\nu}$ be a set of $\binom{\nu}{n}$ nonequivalent generators of the left cosets of the subgroup $\bar{S}^{n}\times\bar{S}^{\nu-n}\subset\bar{S}^{\nu}$ such that

$$\bar{S}^{\nu}=\bar{T}(k_0)\times\bar{S}^{n}\times\bar{S}^{\nu-n} \,. \qquad \text{(A1.26)}$$

Then the elements of $\bar{T}(k_0)$ are the $\binom{\nu}{n}$ permutation operators $\bar{\pi}^{\theta}_{k}\in\bar{S}^{\nu}$ which intercalate the singlet and triplet geminals of the representative (A1.25) without changing their respective relative order. As the singlet geminals enter Serber functions simply as scalar factors, $\bar{\pi}^{\theta}_{k}$ yields another function $\Theta^{2\nu}_{S,M,k}$ of the class. The correspondence between the elements of the class and the permutation operators of $\bar{T}(k_0)$ is unique. According to (A1.15) we have therefore

$$\Theta^{2\nu}_{S,M,k}=\overline{(\pi_k,\pi_k)}^{\sigma}\,\Theta^{2\nu}_{S,M,k_0} \,. \qquad \text{(A1.27)}$$

Consequently the representation matrix of the corresponding permutation (π^{-1}_k, π^{-1}_k) of $T(k_0)\times T(k_0)\subset S^{2\nu}$ is simply

$$V^{S2\nu}_{lk_0}(\pi^{-1}_k, \pi^{-1}_k)=\delta_{l,k} \,, \quad l=1,\ldots,f^{2\nu}_{S} \,. \qquad \text{(A1.28)}$$

H. The representation matrices of the geminal subgroups S^2_{μ}

As mentioned above the Serber representation is fully reduced with respect to the geminal subgroups S^2_{μ} of the intrageminal transpositions $(2\mu-1, 2\mu)$, $\mu=1,\ldots,\nu$. There are only two irreducible representations of S^2, both one dimensional. These are the totally symmetric representation originating from the geminal triplet spin functions corresponding to $S_{2\mu-1,2\mu}=1$ and the totally antisymmetric representation originating from the sin-

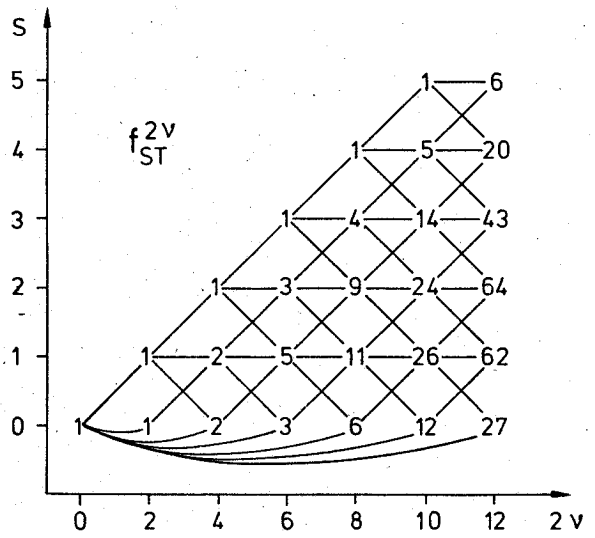

FIG. 5. Branching diagram representing the $f^{2\nu}_{ST}$ [cf. Eq. (A1.23)] different classes $\mathbf{C}^{2\nu}_{S,M}(\underline{k})$ of Serber functions $\Theta^{2\nu}_{S,M,k}$ of t-type $\underline{k}$.

glet spin function corresponding to $S_{2\mu-1,2\mu}=0$. Thus, the representation matrices of all intrageminal permutations are diagonal:

$$V^{S^{2\nu}}_{kk'}(2\mu-1,2\mu)=\epsilon(k,\mu)\delta_{k,k'} \tag{A1.29a}$$

with

$$\epsilon(k,\mu)=\begin{cases}+1 & \text{if} \quad S_{2\mu-1,2\mu}=1\\ -1 & \text{if} \quad S_{2\mu-1,2\mu}=0\end{cases}. \tag{A1.29b}$$

In the following we will show that this simple structure of the representation of the intrageminal permutations is the basis of an important symmetry property of the representation matrices of the subgroup $S^\nu \times S^\nu$.

I. The "even-odd" symmetry of the subduced representation of $S^\nu \times S^\nu$

Theorem A1.1: The Serber representation matrices of the subgroup $S^\nu \times S^\nu$ (A1.14) of $S^{2\nu}$ have the property

$$V^{S^{2\nu}}_{kk'}(p,\tilde{p})=\alpha(k,k')V^{S^{2\nu}}_{kk'}(\tilde{p},p) \tag{A1.30a}$$

with

$$\alpha(k,k')=\pm 1\ . \tag{A1.30b}$$

The signs $\alpha(k,k')$ are given by

$$\alpha(k,k')=\alpha_0(k)\alpha_0(k')\ , \tag{A1.30c}$$

where $\alpha_0(k)$ and $\alpha_0(k')$ are the *parities* of the Serber functions $\Theta^{2\nu}_{S,M,k}$ and $\Theta^{2\nu}_{S,M,k'}$, respectively, with respect to a reference Serber function $\Theta^{2\nu}_{S,M,k_0}$, the parity $\alpha_0(k_0)$ of which is set

$$\alpha_0(k_0)=1\ . \tag{A1.30d}$$

The proof of this theorem will be given further below. According to Theorem A1.1 one can obtain the parities $\alpha_0(k)$ of the $f^{2\nu}_S$ Serber functions $\Theta^{2\nu}_{S,M,k}$ with respect to the reference function $\Theta^{2\nu}_{S,M,k_0}$ in the following way: Let $(p,\tilde{p})$ be a permutation of $S^\nu \times S^\nu \subset S^{2\nu}$ for which the matrix element $V^{S^{2\nu}}_{k_0k}(p,\tilde{p})$ does not vanish. Then $V^{S^{2\nu}}_{k_0k}(\tilde{p},p)$ is also different from zero and the parity $\alpha_0(k)$ is

$$\alpha_0(k)=V^{S^{2\nu}}_{k_0k}(p,\tilde{p})/V^{S^{2\nu}}_{k_0k}(\tilde{p},p)\ . \tag{A1.31}$$

The parity of a Serber function is "t-type invariant," i.e., the parities of the functions in a given class $\mathbf{C}^{2\nu}_{S,M}(k)$ are identical. To show this let $\Theta^{2\nu}_{S,M,l_0}$ with parity $\alpha_0(l_0)$ be the representative of the class $\mathbf{C}^{2\nu}_{S,M}(l)$, let $\Theta^{2\nu}_{S,M,l}$ with parity $\alpha_0(l)$ be another element of this class and let $V^{S^{2\nu}}_{k_0l}(p,\tilde{p})$ be a nonvanishing matrix element. Then from (A1.28)

$$\begin{aligned}V^{S^{2\nu}}_{k_0l}(p,\tilde{p})&=\sum_{l'}V^{S^{2\nu}}_{k_0l'}(p,\tilde{p})V^{S^{2\nu}}_{l'l_0}(\pi_l^{-1},\pi_l^{-1})\\ &=V^{S^{2\nu}}_{k_0l_0}(p\pi_l^{-1},\tilde{p}\pi_l^{-1})\ .\end{aligned} \tag{A1.32}$$

Obviously this relation also holds for the matrix element of the permutation $(\tilde{p},p)$ such that the quotients $\alpha_0(l)$ and $\alpha_0(l_0)$ of these matrix elements are identical.

The "even-odd" symmetry property of the Serber representation of the subgroup $S^\nu \times S^\nu$ stated by Theorem A1.1 implies that the representation matrix of $(p,\tilde{p})$, with $p(\tilde{p})$ a permutation of the odd (even) indices, up to signs is equal to the representation matrix of $(\tilde{p},p)$. The signs are determined by the $f^{2\nu}_{ST}$ parities of the t-type representatives. Thus the $(\nu!)^2$ representation matrices of the subgroup $S^\nu \times S^\nu$ can be generated readily from a much smaller subset of $\frac{1}{2}\nu!(\nu!+1)$ representation matrices and from $f^{2\nu}_{ST}$ parities. As a result Theorem A1.1 provides a prescription for the "even-odd symmetrical" storage of the representation of the subgroup $S^\nu \times S^\nu \subset S^{2\nu}$.

The proof of Theorem A1.1 is based on two auxiliary theorems:

Theorem A1.2: If the representation matrix element $V^{S^{2\nu}}_{kk'}(2\mu,2\mu+1)$ of the *intergeminal* transposition $(2\mu, 2\mu+1)$ between the μth and the $(\mu+1)$th geminal pair does not vanish for a given pair of Serber functions $\Theta^{2\nu}_{S,M,k}$ and $\Theta^{2\nu}_{S,M,k'}$, then the product

$$\alpha(k,k',\mu)=\epsilon(k,\mu)\epsilon(k',\mu)\epsilon(k,\mu+1)\epsilon(k',\mu+1) \tag{A1.33}$$

of the elements of the representation matrices (A1.29) of the corresponding *intrageminal* transpositions is independent of μ:

$$[V^{S^{2\nu}}_{kk'}(2\mu,2\mu+1)\neq 0 \Rightarrow \alpha(k,k',\mu)=\alpha(k,k')]\ ,\quad \mu=1,\ldots,\nu\ . \tag{A1.34}$$

Proof: Suppose for a certain $\mu_0 \in \{1,\ldots,\nu\}$ and a given pair of Serber functions we have

$$V^{S^{2\nu}}_{kk'}(2\mu_0,2\mu_0+1)\neq 0\ . \tag{A1.35}$$

From the orthogonality of the spin geminals (A1.3) for the genealogies k and k' follows then

$$S_{2\mu-1,2\mu}=S'_{2\mu-1,2\mu} \quad \text{for} \quad \mu>\mu_0+1 \quad \text{and} \quad \mu<\mu_0 \tag{A1.36a}$$

or by virtue of (A1.29)

$$\epsilon(k,\mu)=\epsilon(k',\mu) \quad \text{for} \quad \mu\notin\{\mu_0,\mu_0+1\}\ . \tag{A1.36}$$

Suppose now that there is a $\mu_1\neq\mu_0$ such that we also have

$$V^{S^{2\nu}}_{kk'}(2\mu_1,2\mu_1+1)\neq 0\ . \tag{A1.37}$$

Then we obtain similarly

$$S_{2\mu-1,2\mu}=S'_{2\mu-1,2\mu} \quad \text{for} \quad \mu>\mu_1+1 \quad \text{and} \quad \mu<\mu_1 \tag{A1.38a}$$

$$\epsilon(k,\mu)=\epsilon(k',\mu) \quad \text{for} \quad \mu\notin\{\mu_1,\mu_1+1\}\ . \tag{A1.38b}$$

There are now two possibilities:

(i) For $\mu_1\neq\mu_0\pm 1$ we get immediately from (A1.36) and (A1.38)

$$\epsilon(k,\mu)=\epsilon(k',\mu) \quad \mu=1,\ldots,\nu\ . \tag{A1.39}$$

According to (A1.29b) and (A1.33) we obtain for every μ

$$\alpha(k,k',\mu)=1 \tag{A1.40}$$

such that (A1.34) is valid.

(ii) For $\mu_1=\mu_0\pm 1$ we may consider without loss of generality $\mu_1=\mu_0+1$. Then by virtue of (A1.36) and (A1.38)

$$\epsilon(k,\mu)=\epsilon(k',\mu) \quad \text{for} \quad \mu\neq\mu_0+1 \tag{A1.41}$$

and we conclude from (A1.29b) and (A1.33)

$$\alpha(k,k',\mu_0)=\alpha(k,k',\mu_1)\ . \tag{A1.42}$$

Theorem A1.3: Let the genealogy symbols k, k', k'' denote three Serber functions for which the product

$$V^{S2\nu}_{kk'}(2\mu, 2\mu+1)V^{S2\nu}_{k'k''}(2\lambda, 2\lambda+1) \tag{A1.43}$$

of the elements of the representation matrices of two intergeminal transpositions does not vanish. Then the product $\alpha(k,k')\alpha(k',k'')$ is independent of k' and

$$\alpha(k,k'')=\alpha(k,k')\alpha(k',k'') \ . \tag{A1.44}$$

The proof of this property is based on similar and equally simple considerations like the proof of the foregoing theorem and can be found in Ref. 30.

We can now easily prove Theorem A1.1. Let $\Theta^{2\nu}_{S,M,k_0}$ be one of the $f^{2\nu}_S$ Serber functions. Then

$$\alpha_0(k)=\alpha(k_0,k) \tag{A1.45}$$

defines a functional, which attaches to every Serber function $\Theta^{2\nu}_{S,M,k}$ a number $\alpha_0(k)=\pm 1$. We call $\alpha_0(k)$ the *parity* of $\Theta^{2\nu}_{S,M,k}$ with respect to the reference function $\Theta^{2\nu}_{S,M,k_0}$. Because of Theorem A1.3 we have

$$\alpha(k,k')=\alpha_0(k)\alpha_0(k') \ . \tag{A1.46}$$

Theorem A1.2 is equivalent to the identity

$$[\epsilon(k,\mu)\epsilon(k',\mu)\epsilon(k,\mu+1)\epsilon(k',\mu+1)-\alpha(k,k')] \times V^{S2\nu}_{kk'}(2\mu,2\mu+1)=0 \ . \tag{A1.47a}$$

This expression according to (A1.29a) is equivalent to

$$V^{S2\nu}_{kk'}(2\mu-1,2\mu+1)=\alpha(k,k')V^{S2\nu}_{kk'}(2\mu,2\mu+2) \tag{A1.47b}$$

from which we obtain through (A1.13) and (A1.14):

$$V^{S2\nu}_{kk'}[(\mu,\mu+1),e] =\alpha(k,k')V^{S2\nu}_{kk'}[e,(\mu,\mu+1)] \ . \tag{A1.47c}$$

By virtue of (A1.46) and (A1.47) one can show that (A1.30a) holds for any pair of neighbor transpositions $[(\mu,\mu+1),(\lambda,\lambda+1)]$ of $S^\nu \times S^\nu$. But since one can represent every permutation of $S^\nu \times S^\nu$ as a product of such transpositions one concludes further using again (A1.46) [or equivalently (A1.44)] that (A1.30a) is true for all permutations of the subgroup $S^\nu \times S^\nu$.

APPENDIX II: COMMUTATORS OF THE HAMILTONIAN

In this Appendix we will prove Eq. (4.8) for the operators $\hat{H}_{\eta\xi}$ belonging to the classes (4.5g) and (4.5h). For this purpose some commutator identities will be needed.

Arbitrary operators H, S satisfy

$$[H_1H_2,S]=[H_1,[H_2,S]]+[H_1,S]H_2+[H_2,S]H_1 \ . \tag{A2.1}$$

In case $[H_1,S]=0$ one has

$$[H_1H_2,S]=H_1[H_2,S] \ . \tag{A2.2}$$

If a set of operators H_i $(i=1,2,\ldots)$ and a set of mutually commuting operators S_ν $(\nu=1,2,\ldots)$ have commutation relations of the form

$$[H_i,S_\nu]=c_{i\nu}S_{i\nu} \tag{A2.3a}$$

where the coefficients $c_{i\nu}$ are scalar factors and the operators $S_{i\nu}$ commute with S_ν, then

$$[H_i,S_1S_2\cdots S_\nu]=\sum_{\mu=1}^{\nu}c_{i\mu}S_{i\mu}\prod_{\substack{\kappa=1\\ \kappa\neq\mu}}^{\nu}S_\kappa \ , \tag{A2.3b}$$

$$[H_j,[H_i,S_1S_2\cdots S_\nu]]=\sum_{\substack{\mu,\lambda=1\\ \lambda\neq\mu}}^{\nu}c_{i\mu}c_{j\lambda}S_{i\mu}S_{j\lambda}\prod_{\substack{\kappa=1\\ \kappa\neq\mu,\lambda}}^{\nu}S_\kappa +\sum_{\mu=1}^{\nu}c_{i\mu}[H_j,S_{i\mu}]\prod_{\substack{\kappa=1\\ \kappa\neq\mu}}^{\nu}S_\kappa \ . \tag{A2.3c}$$

Commutators of the operators (4.5g) with IP's of single excitations

The commutators of the particle and hole shift operators collected in (4.5g) with single excitation operators are

$$[{}^{0,0}P^{+l}_m,{}^{S,M}S^{+ni}]=\frac{1}{\sqrt{2}}\delta_{m,n}\,{}^{S,M}S^{+li} \ , \tag{A2.4a}$$

$$[{}^{0,0}H^{+i}_j,{}^{S,M}S^{+lk}]=-\frac{1}{\sqrt{2}}\delta_{j,k}\,{}^{S,M}S^{+li} \ . \tag{A2.4b}$$

These commutators are of the form (A2.3a). Since, furthermore, all single excitation operators ${}^{S,M}S^{+li}$ commute with each other, one can calculate the commutators of the operators ${}^{0,0}H^{+j}_k$ and ${}^{0,0}P^{+l}_m$ with ν-fold products of spin-coupled single excitation operators according to (A2.3b) and (A2.3c). The AIP's ${}^{S,M}_kB^+_\nu$ (3.13) in the Serber coupling scheme are linear combinations of such ν-fold products

$${}^{S,M}_kB^+_\nu=\sum_{M_1\cdots M_\nu}{}^{S,M}_kD_{M_1\cdots M_\nu}\prod_{\kappa=1}^{\nu}{}^{S_\kappa,M_\kappa}S^{+l_\kappa i_\kappa} \ . \tag{A2.5}$$

Furthermore, the commutators (A2.4) do not affect the spins (S_κ,M_κ) but only the orbital configurations (l_κ,i_κ) of the single excitations changing one of the orbital indices. By virtue of (A2.3b) one obtains

$$[{}^{0,0}P^{+m}_n,{}^{S,M}_kB^+_\nu]=\frac{1}{\sqrt{2}}\sum_{\mu=1}^{\nu}\delta_{n,l_\mu}\,{}^{S,M}_kB^+_\nu(m,l_\mu) \ , \tag{A2.6a}$$

the AIP ${}^{S,M}_kB^+(m,l_\mu)$ given by (4.12). Similarly one finds for the commutator of the hole shift operator

$$[{}^{0,0}H^{+j}_k,{}^{S,M}_kB^+_\nu]=-\frac{1}{\sqrt{2}}\sum_{\mu=1}^{\nu}\delta_{k,i_\mu}\,{}^{S,M}_kB^+_\nu(j,i_\mu) \ . \tag{A2.6b}$$

Since single excitation operators commute with each other one can calculate using Eq. (A2.2) the commutators of the AIP's (A2.5) with the operator products ${}^{0,0}S^{+li}\,{}^{0,0}P^{+m}_n$ and ${}^{0,0}S^{+li}\,{}^{0,0}H^{+j}_k$ of (4.5g). Multiplying (A2.6) by ${}^{0,0}S^{+li}$ one obtains [cf. (4.9)]

$${}^{S,M}_{\tilde{k}}B^+_{\nu+1}(li,(m,l_\mu))={}^{0,0}S^{+li}\,{}^{S,M}_kB^+_\nu(m,l_\mu) \ , \tag{A2.7a}$$

$${}^{S,M}_{\tilde{k}}B^+_{\nu+1}(li,(j,i_\mu))={}^{0,0}S^{+li}\,{}^{S,M}_kB^+_\nu(j,i_\mu) \ . \tag{A2.7b}$$

According to (A2.1) the commutator of the AIP's (A2.5) with the binary products of the operators ${}^{0,0}P^{+l}_m$ and ${}^{0,0}H^{+j}_k$ acting on the Fermi vacuum is given by the double commutator (A2.3c) since the latter operators annihilate the Fermi vacuum. One obtains

$$[{}^{0,0}P^{+l}_n,[{}^{0,0}H^{+i}_j,{}^{S,M}_kB^+_\nu]] =-\frac{1}{2}\sum_{\mu,\lambda=1}^{\nu}\delta_{j,i_\mu}\delta_{n,l_\lambda}\,{}^{S,M}_kB^+_\nu((l,l_\lambda),(i,i_\mu)) \tag{A2.8}$$

$$[{}^{0,0}P_o^m, [{}^{0,0}P_m^{+l}, {}^{S,M}_{k}B^+_\nu]]$$
$$= \frac{1}{2}\Big\{\sum_{\substack{\mu,\lambda=1\\ \mu\neq\lambda}}^{\nu} \delta_{m,l_\mu}\delta_{o,l_\lambda}\, {}^{S,M}_{k}B^+_\nu((l,l_\mu),(n,l_\lambda)) + \sum_{\mu=1}^{\nu}\delta_{m,l_\mu}\delta_{o,l}\, {}^{S,M}_{k}B^+_\nu(n,l_\mu)\Big\} \quad \text{(A2.9a)}$$

$$[{}^{0,0}H_k^{+\varepsilon}, [{}^{0,0}H_j^{+i}, {}^{S,M}_{k}B^+_\nu]]$$
$$= \frac{1}{2}\Big\{\sum_{\substack{\mu,\lambda=1\\ \mu\neq\lambda}}^{\nu} \delta_{j,i_\mu}\delta_{k,i_\lambda}\, {}^{S,M}_{k}B^+_\nu((i,i_\mu),(g,i_\lambda)) + \sum_{\mu=1}^{\nu}\delta_{j,i_\mu}\delta_{k,i}\, {}^{S,M}_{k}B^+_\nu(g,i_\mu)\Big\} . \quad \text{(A2.9b)}$$

This proves (4.8) for all operators of the class (4.5g).

Commutators of the operators (4.5h) with IP's of single excitations

Let $Z^\nu \subset S^\nu$ be the set of μ cycles

$$Z^\nu = \{(12\cdots\mu)\in S^\nu \,|\, \mu = 1,2,\ldots,\nu\} . \quad \text{(A2.10)}$$

We can identify each of these μ cycles with the integer μ. The signature $\epsilon(\mu)$ of these μ cycles is

$$\epsilon(\mu) = (-1)^{\mu-1} . \quad \text{(A2.11)}$$

The permutation $(r_{\mu(1)}r_{\mu(2)}\cdots r_{\mu(\nu)})$ of a configuration $(r_1 r_2\cdots r_\nu)$ is given by

$$r_{\mu(\kappa)} = \begin{cases} r_\mu & \kappa = 1 \\ r_{\kappa-1} & 1<\kappa\le\mu \\ r_\kappa & \mu<\kappa\le\nu \end{cases} . \quad \text{(A2.12)}$$

Separation of the first ph pair in the ν-fold product (3.6) of particle and hole creators (3.7) from the remaining ph pairs according to

$$\tilde{A}^+_\nu = \tilde{p}^+_1\tilde{h}^+_1\tilde{A}^+_{\nu-1} \quad \text{(A2.13)}$$

leads to the relation

$$[\tilde{h}_0\tilde{p}_0, \tilde{A}^+_\nu]\,|\,|0\rangle\rangle = \sum_{\mu,\lambda}\epsilon(\mu,\lambda)\overline{(\mu,\lambda)}^{-1}\{\tilde{A}^+_{\nu-1}[\tilde{h}_0\tilde{p}_0,\tilde{p}^+_1\tilde{h}^+_1]\}\,|\,|0\rangle\rangle , \quad \text{(A2.14a)}$$

where

$$\overline{(\mu,\lambda)}^{-1}\{\tilde{A}^+_{\nu-1}[\tilde{h}_0\tilde{p}_0,\tilde{h}^+_1\tilde{p}^+_1]\} = \prod_{\kappa=2}^{\nu}\tilde{p}^+_{\mu(\kappa)}\tilde{h}^+_{\lambda(\kappa)}[\tilde{h}_0\tilde{p}_0,\tilde{p}^+_{\mu(1)}\tilde{h}^+_{\lambda(1)}] . \quad \text{(A2.14b)}$$

To show this we note that one obtains from (A2.1) and Wick's theorem (omitting the "~" for the sake of simplicity)

$$[h_0 p_0, A^+_\nu]\,|\,|0\rangle\rangle = \sum_{\mu=1}^{\nu}[p_0,p^+_\mu]_+[h_0,p^+_1h^+_1\cdots p^+_{\mu-1}h^+_{\mu-1}h^+_\mu p^+_{\mu+1}h^+_{\mu+1}\cdots h^+_\nu]\,|\,|0\rangle\rangle .$$

A permutation of the first $\mu-1$ ph creators yields

$$\sum_{\mu=1}^{\nu}(-1)^{\mu-1}[p_0,p^+_\mu]_+ \times[h_0,h^+_1p^+_1\cdots h^+_{\mu-1}p^+_{\mu-1}h^+_\mu p^+_{\mu+1}h^+_{\mu+1}\cdots h^+_\nu]\,|\,|0\rangle\rangle .$$

Applying Wick's theorem again and permuting the first $\lambda-1$ hp creators yields

$$\sum_{\mu=1}^{\nu}(-1)^{\mu-1}[p_0,p^+_\mu]_+\Big\{\sum_{\lambda=1}^{\mu-1}(-1)^{\lambda-1}[h_0,h^+_\lambda]_+p^+_1h^+_1\cdots p^+_{\lambda-1}h^+_{\lambda-1}p^+_\lambda h^+_{\lambda+1}\cdots p^+_{\mu-2}h^+_{\mu-1}p^+_{\mu-1}h^+_\mu p^+_{\mu+1}\cdots h^+_\nu + (-1)^{\mu-1}[h_0,h^+_\mu]_+p^+_1h^+_1\cdots p^+_{\mu-1}h^+_{\mu-1}p^+_{\mu+1}h^+_{\mu+1}\cdots h^+_\nu + \sum_{\lambda=\mu+1}^{\nu}(-1)^{\lambda-1}[h_0,h^+_\lambda]_+p^+_1h^+_1\cdots p^+_{\mu-1}h^+_{\mu-1}p^+_{\mu+1}h^+_\mu\cdots p^+_\lambda h^+_{\lambda-1}p^+_{\lambda+1}h^+_{\lambda+1}\cdots h^+_\nu\Big\}\,|\,|0\rangle\rangle .$$

Application of (A2.11), (A2.12), (2.5), and of the identity

$$[h_0p_0,p^+_\mu h^+_\lambda]\,|\,|0\rangle\rangle = [p_0,p^+_\mu]_+[h_0,h^+_\lambda]_+\,|\,|0\rangle\rangle$$

completes the proof.

Decomposing the permutation operator $\overline{P}\in\overline{S}^{2\nu}$ into a product of $\overline{P}^\tau$ and $\overline{P}^\sigma$, acting separately on the space and spin part of an AIP (3.13), respectively, one obtains from (A1.10)

$$\overline{P}^{-1}\, {}^{S,M}_{k}B^+_\nu = \sum_{k'} V^{S2\nu}_{k'k}(p)\,\overline{P}^{\tau-1}\, {}^{S,M}_{k'}B^+_\nu . \quad \text{(A2.15)}$$

Representation of the Serber-coupled AIP's (3.13) in terms of IP's of single excitations according to (A2.5) yields by virtue of (A2.14a) and (A2.15)

$$[{}^{0,0}S_{jm}, {}^{S,M}_{k}B^+_\nu]\,|\,|0\rangle\rangle = \sum_{\mu,\lambda}\sum_{k'}\epsilon(\mu,\lambda)V^{S2\nu}_{k'k}(\mu,\lambda)\overline{(\mu,\lambda)}^{\tau-1}\sum_{M_1\cdots M_\nu}\, {}^{S,M}_{k'}D_{M_1\cdots M_\nu}\prod_{\kappa=1}^{\nu}\, {}^{s_\kappa,M_\kappa}S^{+l_\kappa i_\kappa}[{}^{0,0}S_{jm}, {}^{s_1,M_1}S^{+l_1i_1}]\,|\,|0\rangle\rangle . \quad \text{(A2.16)}$$

The commutator in the last term is found to be

$$[{}^{0,0}S_{jm}, {}^{s,M}S^{+it}]\,|\,|0\rangle\rangle = \delta_{s,0}\delta_{m,t}\delta_{j,i}\,|\,|0\rangle\rangle . \quad \text{(A2.17)}$$

Therefore, only those terms contribute in (A2.16) to the sum over k' for which the genealogy symbol k' (A1.2) contains a first geminal pair of singlet character. The functional $\tau(k')$ defined by (4.15b) is equal to one in this case, and zero otherwise. If $\tau(k')=1$ one has

$$ {}^{S,M}_{k'}B^{+}_{\nu} = {}^{0,0}S^{+I_1 i_1}\ {}^{S,M}_{\tilde{k}'}[l^{+}_2 i^{+}_2 \cdots l^{+}_\nu i^{+}_\nu] \ . \tag{A2.18} $$

From (1.21), (A2.12), (A2.14b), and (A2.16)–(A2.18) one concludes

$$ [{}^{0,0}S_{jm},\ {}^{S,M}_{k}B^{+}_{\nu}]\,|\,|0\rangle\rangle = \sum_{\mu,\lambda}\sum_{k'} U^{S2\nu}_{k'k}(\mu,\lambda)\tau(k')\delta_{m,l_\mu}\delta_{j,i_\lambda}\ {}^{S,M}_{\tilde{k}'}[l^{+}_{\mu(2)} i^{+}_{\lambda(2)} \cdots l^{+}_{\mu(\nu)} i^{+}_{\lambda(\nu)}] \ . $$

Multiplication with ${}^{0,0}S^{+I\bar{I}}$ and application of relations (A2.18), (A2.12), (2.31), and (4.12) yields

$$ {}^{0,0}S^{+I\bar{I}}[{}^{0,0}S_{jm},\ {}^{S,M}_{k}B^{+}_{\nu}]\,|\,|0\rangle\rangle = \sum_{\mu,\lambda}\delta_{m,l_\mu}\delta_{j,i_\lambda}\sum_{k'} U^{S2\nu}_{k'k}(\mu,\lambda)\tau(k')\overline{(\mu,\lambda)}^{\nu-1}\ {}^{S,M}_{k'}B^{+}_{\nu}[(l,l_\mu),(i,i_\lambda)]\,|\,|0\rangle\rangle \ . $$

In order to represent the ν-fold excitation operators ${}^{S,M}_{k'}B^{+}_{\nu}$ by their t-type representatives ${}^{S,M}_{k_0}B^{+}_{\nu}$ one makes use of the relations (cf. Appendix IG)

$$ {}^{S,M}_{k'}B^{+}_{\nu} = \overline{(\pi_{k'},\pi_{k'})}^{\nu-1}\ {}^{S,M}_{k_0}B^{+}_{\nu} $$

and

$$ V^{S2\nu}_{k_0 k}(\pi_{k'}\mu,\pi_{k'}\lambda) = V^{S2\nu}_{k'k}(\mu,\lambda) $$

where the t-type preserving permutations are the elements of the set $T(k_0)\subset S^{\nu}$ (A1.26). This yields the final result

$$ {}^{0,0}S^{+I\bar{I}}[{}^{0,0}S_{jm},\ {}^{S,M}_{k}B^{+}_{\nu}]\,|\,|0\rangle\rangle $$

$$ = \sum_{\mu,\lambda}\delta_{m,l_\mu}\delta_{j,i_\lambda}\sum_{k_0=1}^{f^{2\nu}_{ST}}\sum_{\pi_{k'}\in T(k_0)} U^{S2\nu}_{k_0 k}(\pi_{k'}\mu,\pi_{k'}\lambda)\tau(k')\overline{(\pi_{k'}\mu,\pi_{k'}\lambda)}^{\nu-1}\ {}^{S,M}_{k_0}B^{+}_{\nu}((l,l_\mu),(i,i_\lambda))\,|\,|0\rangle\rangle \ . \tag{A2.19} $$

(A2.19) proves (4.8) for the operators of the class (4.5h).

APPENDIX III: PROOF OF THE MATRIX ELEMENT FORMULA (4.39e)

We assume that condition (4.34e) holds, i.e.,

$$ \mathbf{L} - (\mathbf{L}\cap\mathbf{M}) = \{l_{\mu_1}, l_{\mu_2}\} \tag{A3.1} $$

and

$$ \mathbf{I} = \mathbf{J} \tag{A3.2} $$

such that

$$ \mathbf{M} - (\mathbf{M}\cap\mathbf{L}) = \{m_{\rho_1}, m_{\rho_2}\} \ . \tag{A3.3} $$

We will consider one by one the various terms $|\eta\zeta\rangle$ [cf. (4.26)] in the expansion (4.11d). These terms give a nonvanishing contribution only if condition (4.33) is valid for the corresponding orbital index sets, i.e., if $\{\mathbf{M},\mathbf{J}\}$ and $\{\tilde{\mathbf{L}}(\eta\zeta),\tilde{\mathbf{I}}(\eta\zeta)\}$ are identical.

For the term $|01\rangle$

$$ \{\mathbf{M},\mathbf{J}\} \neq \{\tilde{\mathbf{L}}(01),\tilde{\mathbf{I}}(01)\} \ . \tag{A3.4} $$

Proof: The assumption $\tilde{\mathbf{L}}(01)=\mathbf{M}$ leads to a contradiction because of

$$ \{l_{\mu_1}, l_{\mu_2}\} = \mathbf{L} - (\mathbf{L}\cap\mathbf{M}) = \tilde{\mathbf{L}}(01) - (\tilde{\mathbf{L}}(01)\cap\mathbf{M}) = \emptyset \ , $$

where (A3.1) and (4.29a) have been used.

Similarly one may show that all the other terms $|02\rangle - |04\rangle$ and $|06\rangle$ cannot give a contribution to the matrix element.

For $|05\rangle$

$$ (4.33) \Leftrightarrow [\{l_{\mu_1}, l_{\mu_2}\} = \{l_\mu, l_\lambda\} \tag{A3.5} $$

and

$$ \{m_{\rho_1}, m_{\rho_2}\} = \{n, l\}] \ . $$

Proof: Because of (A3.2) and (4.29e)

$$ (4.33) \Leftrightarrow \tilde{\mathbf{L}}(05) = \mathbf{M} \ , $$

i.e., the asserted equivalence has to be proved for the latter condition.

"$\Leftarrow$": From the assumption $\{l_{\mu_1}, l_{\mu_2}\} = \{l_\mu, l_\lambda\}$ we obtain according to (4.29e)

$$ \tilde{\mathbf{L}}(05) = (\mathbf{L} - \{l_{\mu_1}, l_{\mu_2}\}) \cup \{n, l\} = (\mathbf{L} - (\mathbf{L} - (\mathbf{L}\cap\mathbf{M}))) \cup \{n, l\} $$
$$ = (\mathbf{L}\cap\mathbf{M}) \cup \{n, l\} = (\mathbf{M} - \{m_{\rho_1}, m_{\rho_2}\}) \cup \{n, l\} $$

such that $\{m_{\rho_1}, m_{\rho_2}\} = \{n, l\} \Rightarrow \tilde{\mathbf{L}}(05) = \mathbf{M}$.

"$\Rightarrow$": From the assumption $\mathbf{M} = \tilde{\mathbf{L}}(05)$ one obtains

$$ \{l_{\mu_1}, l_{\mu_2}\} = \mathbf{L} - (\mathbf{L}\cap\mathbf{M}) = \mathbf{L} - (\mathbf{L}\cap((\mathbf{L} - \{l_\mu, l_\lambda\}) \cup \{n, l\})) $$
$$ = \mathbf{L} - ((\mathbf{L} - \{l_\mu, l_\lambda\}) \cup (\mathbf{L}\cap\{n, l\})) $$
$$ = \{l_\mu, l_\lambda\} - (\{l_\mu, l_\lambda\}\cap\{n, l\}) \subset \{l_\mu, l_\lambda\} $$
$$ \Rightarrow \{l_{\mu_1}, l_{\mu_2}\} = \{l_\mu, l_\lambda\} \ . $$

Similarly one may prove the second part of the proposition.

For the matrix element expansion we obtain now from (4.11c)

$$ \langle {}^{S,M}_{k}B^{+}_{\nu}\,|\,\hat{H}\,|\,{}^{S,M}_{k_2}B^{+}_{\nu}\rangle $$

$$ = \sum_{\mu<\lambda}\sum_{l,n}(ll_\mu\,|\,nl_\lambda)\langle {}^{S,M}_{k_1}B^{+}_{\nu}\,|\,{}^{S,M}_{k_2}B^{+}_{\nu}((l,l_\mu),(n,l_\lambda))\rangle \tag{A3.6} $$

where only those terms do not vanish for which condition (A3.5) holds.

We consider first the reduction of the summation induced by the condition $\{l,n\} = \{m_{\rho_1}, m_{\rho_2}\}$. If $m_{\rho_1} = m_{\rho_2}$ then

$$\sum_{l,n}(ll_\mu|nl_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((l,l_\mu),(n,l_\lambda))\rangle=(m_{\rho_1}l_\mu|m_{\rho_1}l_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((m_{\rho_1},l_\mu),(m_{\rho_1},l_\lambda))\rangle$$

$$=\tfrac{1}{2}\{(m_{\rho_1}l_\mu|m_{\rho_2}l_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((m_{\rho_1},l_\mu),(m_{\rho_2},l_\lambda))\rangle+(m_{\rho_2}l_\mu|m_{\rho_1}l_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((m_{\rho_2},l_\mu),(m_{\rho_1},l_\lambda))\rangle\}\,. \tag{A3.7}$$

If $m_{\rho_1}\neq m_{\rho_2}$ then one obtains up to a factor $\frac{1}{2}$ the same result. Using the function ξ [cf. (4.37)] one finds

$$\langle {}^{S,M}_{k_1}B^+_\nu|\hat{H}|{}^{S,M}_{k_2}B^+_\nu\rangle=\xi(m_{\rho_1},m_{\rho_2})\sum_{\mu<\lambda}\{(m_{\rho_1}l_\mu|m_{\rho_2}l_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((m_{\rho_1},l_\mu),(m_{\rho_2},l_\lambda))\rangle$$

$$+(m_{\rho_2}l_\mu|m_{\rho_1}l_\lambda)\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((m_{\rho_2},l_\mu),(m_{\rho_1},l_\lambda))\rangle\}\,. \tag{A3.8}$$

Next we consider the reduction of the summation induced by the condition $\{l_\mu,l_\lambda\}=\{l_{\mu_1},l_{\mu_2}\}$. If $l_{\mu_1}=l_{\mu_2}$ the summation index sets $[\mu_1]$ and $[\mu_2]$ (4.38a) are identical: $[\mu_1]=[\mu_2]=\{\mu_1,\mu_2\}$. Using the symmetry properties

$$(m_{\rho_1}l_{\mu_1}|m_{\rho_2}l_{\mu_2})=(m_{\rho_2}l_{\mu_2}|m_{\rho_1}l_{\mu_1}) \tag{A3.9}$$

and

$${}^{S,M}_{k}B^+_\nu((m_{\rho_1},l_{\mu_1}),(m_{\rho_2},l_{\mu_2}))={}^{S,M}_{k}B^+_\nu((m_{\rho_2},l_{\mu_2}),(m_{\rho_1},l_{\mu_1})) \tag{A3.10}$$

and assuming without loss of generality $\mu_1<\mu_2$ we find

$$\langle {}^{S,M}_{k_1}B^+_\nu|\hat{H}|{}^{S,M}_{k_2}B^+_\nu\rangle=\xi(m_{\rho_1},m_{\rho_2})\Big\{(m_{\rho_1}l_{\mu_1}|m_{\rho_2}l_{\mu_2})\sum_{\mu\in[\mu_1]}\sum_{\substack{\lambda\in[\mu_2]\\ \lambda\neq\mu}}\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((m_{\rho_1},l_\mu),(m_{\rho_2},l_\lambda))\rangle$$

$$+(m_{\rho_2}l_{\mu_1}|m_{\rho_1}l_{\mu_2})\sum_{\mu\in[\mu_1]}\sum_{\substack{\lambda\in[\mu_2]\\ \lambda\neq\mu}}\langle {}^{S,M}_{k_1}B^+_\nu|{}^{S,M}_{k_2}B^+_\nu((m_{\rho_2},l_\mu),(m_{\rho_1},l_\lambda))\rangle\Big\}\,. \tag{A3.11}$$

If $l_{\mu_1}\neq l_{\mu_2}$ the summation index sets $[\mu_1]$ and $[\mu_2]$ are disjoint. Thus the condition $\{l_\mu,l_\lambda\}=\{l_{\mu_1},l_{\mu_2}\}$ holds for all $\mu\in[\mu_1]$ and $\lambda\in[\mu_2]$ and the matrix element expression reduces, up to a factor $\frac{1}{2}$, to the expression above. This is obvious if $\mu<\lambda$ for all $\mu\in[\mu_1]$ and $\lambda\in[\mu_2]$. Otherwise it can be verified easily by means of the symmetry properties (A3.9) and (A3.10). Introduction of a factor $\xi(l_{\mu_1},l_{\mu_2})$ accounting for the factor $\frac{1}{2}$ yields the matrix element formula (4.39e).

[1] P. J. A. Ruttink, Theor. Chim. Acta 49, 223 (1978).
[2] J. C. Slater, Phys. Rev. 34, 1293 (1929).
[3] J. C. Slater, Phys. Rev. 38, 1109 (1931).
[4] E. U. Condon, Phys. Rev. 36, 1121 (1930).
[5] J. Čižek, Theor. Chim. Acta 6, 292 (1966).
[6] J. N. Murrell and K. L. McEwen, J. Chem. Phys. 25, 1143 (1956).
[7] H. Ito and Y. I'Haya, Theor. Chim. Acta 2, 247 (1964).
[8] M. Nakayama and Y. I'Haya, Int. J. Quantum Chem. 4, 43 (1970).
[9] M. Yamazaki, Sci. Rep. of Kanazawa University 8, 397 (1963).
[10] J. Paldus, B. G. Adams, and J. Čižek, Int. J. Quantum Chem. 11, 813 (1977).
[11] B. G. Adams, J. Paldus, and J. Čižek, Int. J. Quantum Chem. 11, 849 (1977).
[12] R. R. Luchese and H. F. Schaefer III, J. Chem. Phys. 68, 769 (1978).
[13] K. Ruedenberg, Phys. Rev. Lett. 27, 1105 (1971).
[14] K. Ruedenberg and R. D. Poshusta, Adv. Quantum Chem. 6, 267 (1972).
[15] W. I. Salmon and K. Ruedenberg, J. Chem. Phys. 57, 2776 (1972).
[16] J. Karwowski, Theor. Chim. Acta 29, 151 (1973).
[17] I. G. Kaplan, *Symmetry of Many-Electron Systems* (Academic, New York, 1975).
[18] I. M. Gelfand and M. L. Tsetlin, Dok. Akad. Nauk USSR 71, 825 (1950).
[19] M. Moshinsky, J. Math. Phys. 4, 1128 (1953).
[20] J. Paldus, in *Theoretical Chemistry: Advances and Perspectives*, edited by H. Eyring and D. J. Henderson (Academic, New York, 1976), Vol. 2, p. 131.
[21] F. A. Matsen, Int. J. Quantum Chem. 58, 379 (1974).
[22] G. A. Segal, R. W. Wetmore, and K. Wolf, Chem. Phys. 30, 269 (1978).
[23] I. Shavitt, Int. J. Quantum Chem.: Quantum Chem. Symp. 11, 131 (1977).
[24] I. Shavitt, Int. J. Quantum Chem.: Quantum Chem. Symp. 12, 5 (1978).
[25] B. R. Brooks and H. F. Schaefer III, J. Chem. Phys. 70, 5092 (1979).
[26] P. E. M. Siegbahn, J. Chem. Phys. 70, 5391 (1979).
[27] F. E. Harris, J. Chem. Phys. 46, 2769 (1967); 47, 1047 (1967).
[28] P. Tavan and K. Schulten, J. Chem. Phys. 70, 5407 (1979).
[29] P. Tavan and K. Schulten, J. Chem. Phys. 70, 5414 (1979).
[30] P. Tavan, thesis, Göttingen (1978).
[31] I. Ohmine, M. Karplus, and K. Schulten, J. Chem. Phys. 68, 2298 (1978).
[32] E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic, New York, 1959).
[33] R. Serber, Phys. Rev. 45, 461 (1934); J. Chem. Phys. 2, 697 (1934).
[34] W. Heitler and G. Rumer, Z. Phys. 68, 12 (1931).
[35] L. Pauling, J. Chem. Phys. 1, 280 (1933).
[36] F. A. Matsen, Adv. Quantum Chem. 1, 60 (1960).
[37] F. A. Matsen, A. A. Cantu, and R. D. Poshusta, J. Phys. Chem. 70, 1558 (1966).
[38] A. D. McLachlan, J. Chem. Phys. 33, 663 (1960).
[39] H. Shull, Int. J. Quantum Chem. 3, 523 (1969).
[40] S. F. Boys, Philos. Trans. R. Soc. London 245, 95 (1952).
[41] C. M. Reeves, Commun. ACM 9, 276 (1966).
[42] R. McWeeny, Proc. R. Soc. London Ser. A 223, 63 (1954).
[43] R. McWeeny, "Valence Bond Theory" in *Encyclopedic Dictionary of Physics* (Pergamon, New York, 1961).

[44]I. L. Cooper and R. McWeeny, J. Chem. Phys. 45, 266, 3484 (1966).
[45]B. T. Sutcliffe, J. Chem. Phys. 41, 277 (1966).
[46]P. O. Löwdin, Phys. Rev. 97, 1474, 1509 (1955).
[47]J. K. Percus and A. Rotenberg, J. Math. Phys. 3, 928 (1962).
[48]F. Sasaki and K. Ohno, J. Math. Phys. 4, 1140 (1963).
[49]V. H. Smith, Jr., J. Chem. Phys. 41, 277 (1964).
[50]J. Shapiro, J. Math. Phys. 6, 1680 (1965).
[51]P. A. M. Dirac, Proc. R. Soc. London Ser. A 123, 714 (1929).
[52]T. Yamanouchi, Proc. Phys. Math. Soc. Jpn. 17, 274 (1935); 18, 10, 623 (1936); 19, 436 (1937); 20, 547 (1938); J. Phys. Soc. Jpn. 3, 245 (1948).
[53]M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, "Table of Molecular Integrals," Maruzen, Tokyo (1955).
[54]D. E. Rutherford, *Substitutional Analysis* (Edinburgh Univ., 1948), new edition: (Hafner, New York, 1968).
[55]D. J. Klein, C. H. Carlisle, and F. A. Matsen, Adv. Quantum Chem. 5, 219 (1970).
[56]R. Pauncz, *Alternant Molecular Orbital Method* (Saunders, Philadelphia, 1967).
[57]W. I. Salmon, Adv. Quantum Chem. 8, 37 (1974).
[58]W. I. Salmon, K. Ruedenberg, and I. M. Cheung, J. Chem. Phys. 57, 2787 (1972).
[59]J. Paldus and P. E. S. Wormer, Phys. Rev. A 18, 827 (1978).
[60]H. Horie, J. Phys. Soc. Jpn. 19, 1783 (1964).
[61]S. Wilson, Chem. Phys. Lett. 49, 168 (1977).
[62]U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic, New York, 1959).
[63]A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).
[64]In his book on *Irreducible Tensor Methods* (Academic, New York, 1976) B. L. Silver even warned against the development of such a theory: "Particularly intriguing is the possibility of coupling annihilation and creation operators in the same way as we coupled conventional tensor operators—but this way lie dragons."
[65]B. R. Judd, *Second Quantization and Atomic Spectroscopy* (Johns Hopkins, Baltimore, 1967).
[66]W. H. Greub, *Linear Algebra* (Springer, Berlin, 1963).