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Symmetric-group-based methods in quantum chemistry

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The eigenvalue problem of a Hamiltonian represented in a finite-dimensional model space being the N-electron subspace of the $2K$-spinorbital Fock space is analyzed. It is pointed out that the permutation group $\mathcal{S}_N$ is a very convenient framework for this analysis. The resulting approach is known as the symmetric group approach to the N-electron problem. Its applications to construction of a basis in the model space, to the evaluation of matrix elements of spin-independent and of spin-dependent operators and, finally, to solution of the eigenvalue problem of the Hamiltonian are briefly reviewed. Recently developed applications of the symmetric group to studies of the Heisenberg Hamiltonian spectra and to evaluation of spectral density distribution moments are also dicussed.

1. Introduction

Most of results in the theory of many-particle systems have been obtained using computational techniques derived from an assumption that the Hamiltonian of the system under consideration is defined in a finite-dimensional model space. In the case of a non-relativistic N-electron theory, the space is an antisymmetric and spin-adapted subspace of a finite-dimensional Hilbert space. In the orbital approximation our space, $\mathcal{H}^A(N, K, S, M)$, is the antisymmetric ($A$) and spin-adapted ($S, M$) part of the N-fold tensorial product of $2K$-dimensional one-electron spaces. The N-electron space, frequently referred to as the full configuration interaction (FCI) space, has two kinds of complementary symmetry properties: invariance with respect to unitary transformations of the one-electron basis and invariance with respect to permutations of electrons. Exploiting these two kinds of symmetry resulted in formulating two powerful approaches to the theory of many-electron systems, known as the *Unitary Group Approach* (UGA) and the *Symmetric Group Approach* (SGA) [51].

The importance of the basic duality that exists between the symmetric and the unitary groups for theory of many-electron systems has been emphasized already in the early works of Weyl [74] and Wigner [75]. However, many details of the interrelations between UGA and SGA became clear relatively recently, mainly due to Paldus and Wormer [48,49,76]. SGA, as a general approach to a quantum mechanical description of molecules originates from works of Serber [71], Yamanouchi [78] and Kotani [34, 35]. Papers by Harris [16], opened the way to formulation of general methods of evaluation of matrix elements by Ruedenberg [65] and by the present author [18]. Exploiting the duality of Weyl and the resulting permutational symmetry properties of

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the orbital part of the many-electron wavefunctions, Matsen [41], Klein et al. [31,32] and others developed a formulation known as *spin-free quantum chemistry* (a recent review of this approach has been given by Pauncz [51]). Inspired by the ideas of Shavitt [72] leading to a graphical formulation of UGA (known as GUGA), Duch and Karwowski developed a symmetric group graphical approach (SGGA) [8–10] and applied it to designing large-scale configuration interaction (CI) algorithms [11]. More recently SGA has been applied to many areas of the many-electron system theory including rather exotic ones like, for example, the statistical spectroscopy [53].

Apart from mere applications of the existing mathematical formalism, use of the permutation group in quantum chemistry has resulted in many developments of the basic group-theoretical formulations. A broad review of these topics is given in two monographs by Pauncz [50,51]. Probably the most important in this area are the works of Yamanouchi [78] and Kotani [34,35] on the construction of the irreducible representation matrices. One should also mention contributions of Klein [28] and Matsen [42] to the development of the matric basis of the symmetric group algebra, works on the projection operators [70], on the double cosets [64], on generating representation matrices corresponding to projected spin functions [61], on deriving explicit expressions for the characters [77], just to mention several examples.

In this paper applications of SGA to construction of the N-electron basis in the FCI space [8–10] and to the evaluation of matrix elements of both spin-independent [9,10,18] and spin-dependent [13,17,19] Hamiltonians, to exploring the structure of the model space [8,9,20], to designing configuration interaction methods [21,22], to solving [12,14] and to analyzing [23,25] the eigenvalue problem of the Heisenberg Hamiltonians are discussed. Besides, the use of the permutation group of the orbital indices to evaluate spectral density distribution moments of N-electron systems [24,52,56,57] is briefly reviewed.

2. The model space

The spin-dependent N-electron Hamiltonian $\widehat{H}'$ reads

$$\widehat{H}' = \sum_{i=1}^{N} \widehat{h}_1^{\sigma}(\sigma_i)\widehat{h}_1^{u}(i) + \sum_{i>j}^{N} \widehat{h}_2^{\sigma}(\sigma_i,\sigma_j)\widehat{h}_2^{u}(i,j), \tag{1}$$

where the superscripts σ and u refer, respectively, to the spin- and the space-dependence. For simplicity, the sums in equation (1) are extended over the electron coordinates only rather than over all components of the pertinent spin operators. This simplification does not influence any features of the description which are relevant for our present considerations.

The indistinguishability of electrons is reflected in the invariance of the Hamiltonian with respect to an arbitrary permutation $\widehat{P}$. Similarly, all other quantum me-

chanical observables, in particular the total spin operators $\widehat{S}^2$ and $\widehat{S}_z$, do not change upon a renumbering of electrons. Therefore

$$\left[\widehat{H}', \widehat{P}\right] = \left[\widehat{S}^2, \widehat{P}\right] = \left[\widehat{S}_z, \widehat{P}\right] = 0. \tag{2}$$

This means that the permutation group $\mathcal{S}_N$ is one of the invariance groups of the Hamiltonian and of the total spin operators. According to the Pauli principle, the N-electron wavefunction Ψ transforms according to the antisymmetric representaion of $\mathcal{S}_N$, i.e.,

$$\widehat{P}\Psi = (-1)^p \Psi, \tag{3}$$

where p is the parity of $\widehat{P}$.

In the case of a spin-independent Hamiltonian, equation (1) simplifies to

$$\widehat{H} = \sum_{i=1}^{N} \widehat{h}_1(i) + \sum_{i>j}^{N} \widehat{h}_2(i,j), \tag{4}$$

where $\widehat{h}_1$ includes the kinetic energy and interactions of the electron with an external field (usually with the electrostatic field of the nuclei), and where

$$\widehat{h}_2(i,j) = \frac{1}{r_{ij}} \tag{5}$$

describes the electron–electron interactions between electrons i and j. A spin-independent Hamiltonian is invariant with respect to rotations in spin space. In consequence the Hamiltonian, the square of the total spin operator and its projection form a set of commuting operators

$$\left[\widehat{H}, \widehat{S}^2\right] = \left[\widehat{H}, \widehat{S}_z\right] = \left[\widehat{S}^2, \widehat{S}_z\right] = 0. \tag{6}$$

In the case of a spin-dependent Hamiltonian, the total spin is not a constant of the motion and the commutation relations (6) are not fulfilled.

Let $\langle \sigma | SM, l \rangle$ be an eigenfunction of $\widehat{S}^2$ and $\widehat{S}_z$ which depends only upon spin variables $\sigma = \sigma_1, \sigma_2, \ldots, \sigma_N$ of the N-electron system. The corresponding eigenvector is denoted $|SM, l\rangle$. This means that

$$\widehat{S}^2 |SM, l\rangle = S(S+1)|SM, l\rangle, \tag{7}$$

$$\widehat{S}_z |SM, l\rangle = M|SM, l\rangle, \quad l = 1, 2, \ldots, f, \tag{8}$$

where $l = 1, 2, \ldots, f$ distinguishes independent spin functions belonging to the same S, M pair and [35,50]

$$f \equiv f(S,N) = \frac{2S+1}{N+1} \binom{N+1}{N/2 - S}. \tag{9}$$

The vectors $|SM,l\rangle$, $l = 1,2,\ldots,f$, form a basis in a subspace of the N-electron spin space, which is called the (SM) space. Since $\mathcal{S}_N$ is an invariance group of $\widehat{S}^2$ and $\widehat{S}_z$, their eigenfunctions form bases for its irreducible representations, i.e.,

$$\widehat{P}|SM,l\rangle = \sum_{j=1}^{f} V_S^N(P)_{jl}|SM,j\rangle, \tag{10}$$

where $\mathbf{V_S^N}$ are the matrices of these representations. Index S labels the representation and f is its dimension. Alternatively, the representation may be labelled by a two-row Young shape $[xy]$ in which

$$x = \frac{1}{2}N + S \quad \text{and} \quad y = \frac{1}{2}N - S \tag{11}$$

stand for the lengths of the upper and lower rows, respectively. As one can show [50], the representation matrices are M-independent. If the basis in the (SM) space is chosen orthonormal, then the matrices $\mathbf{V_S^N}$ are orthogonal.

The basis $|SM,l\rangle_{l=1}^{f}$ is complete in the (SM) space. Therefore, every normalized eigenfunction of $\widehat{S}^2$ and $\widehat{S}_z$ which depends upon both spin (σ) and space $(\mathbf{r})$ coordinates of the N electrons may be expanded as

$$\mathbf{\Psi}_{SM}(\mathbf{r},\sigma) = \frac{1}{\sqrt{f}}\sum_{l=1}^{f}\mathbf{\Phi}_{Sl}(\mathbf{r})\langle\sigma|SM,l\rangle, \tag{12}$$

where $\mathbf{\Phi}_{Sl}(\mathbf{r})$ are normalized and M-independent functions of the spatial coordinates of the electrons. If $\mathbf{\Psi}_{SM}(\mathbf{r},\sigma)$ is antisymmetric, then the transformation properties of $\mathbf{\Phi}_{Sl}(\mathbf{r})$ result directly from equations (3) and (10). After some algebra we get

$$\widehat{P}\mathbf{\Phi}_{Sl} = (-1)^p\sum_{j=1}^{f} V_S^N\left(P^{-1}\right)_{lj}\mathbf{\Phi}_{Sj}. \tag{13}$$

The last equation may be rewritten as

$$\widehat{P}\mathbf{\Phi}_{Sl} = \sum_{j=1}^{f} U_S^N(P)_{jl}\mathbf{\Phi}_{Sj}, \tag{14}$$

where

$$\mathbf{U_S^N}(P) = (-1)^p\mathbf{V_S^N}\left(P^{-1}\right)^{\dagger}. \tag{15}$$

Representations $\mathbf{V_S^N}(P)$ and $\mathbf{U_S^N}(P)$ are mutually dual, i.e., they correspond to mutually conjugate Young shapes. Equation (14) says that the orbital parts of antisymmetric eigenfunctions of $\widehat{S}^2$ span a carrier space for the irreducible representation U_S^N of $\mathcal{S}_N$. Therefore instead of introducing spin variables to the wavefunction and imposing the antisymmetry requirement, one can use a spin-independent wavefunction transforming

according to equation (14). This property of N-electron wavefunctions (frequently referred to as the *duality of Weyl*) constitutes a base for the formulation of *spin-free quantum chemistry* [31,32,41].

In order to construct an N-electron basis in the FCI space, we replace $\mathbf{\Phi}$ by a linear combination of the primitive configuration functions taken in the form

$$\mathbf{\Psi}^0_\lambda(\mathbf{r}) = \prod_{i=1}^{N} \psi_{\lambda i}(\mathbf{r}_i), \tag{16}$$

where $\psi_{\lambda i}$ are chosen from an orthonormal set $\psi_1, \psi_2, \ldots, \psi_K$ of orbitals. In the product, which defines the *orbital configuration* λ, s_λ orbitals appear once (singly occupied orbitals or *singles*) and d_λ orbitals – twice (doubly occupied orbitals or *doubles*). The numbers of singles and doubles in λ are connected by the obvious relation

$$s_\lambda + 2d_\lambda = N. \tag{17}$$

We adopt from now on a convention, that in all products of orbitals the position index of an orbital in the product is equal to the designation index of the electron described by this orbital, i.e., if $\psi_{\lambda i}(\mathbf{r}_j)$ is contained in the product, then $i = j$. As a consequence of this convention we usually omit the electron designation indices in the products of orbitals. Besides, for simplicity, we shall write λ_i rather than $\psi_{\lambda i}$ and, whenever it does not lead to any confusion, s/d rather than s_λ/d_λ. We assume that in the orbital products the position indices of singles are always less than those of doubles and that both singles and doubles stand in an ascending order of their indices.

In order to obtain a *symmetric group adapted* basis of configurations one may use appropriate projection operators. If we define a projection operator

$$\mathcal{O}^m_{Sk} = \sqrt{\frac{f(S,N)}{N!\,2^d}} \sum_P U^N_S(P)_{km} \widehat{P}, \tag{18}$$

then

$$\mathbf{\Phi}^{(m)}_{Sk} = \mathcal{O}^m_{Sk} \mathbf{\Psi}^0_\lambda(\mathbf{r}) \tag{19}$$

form an orthonormal set and fulfill equation (14) for $m \leqslant f(S,s)$ and vanish for $m > f(S,s)$ [35,51]. Substituting the above result into equation (12) we get, for each configuration λ, a set of $f(S,s)$ antisymmetric and spin-adapted *configuration state functions* (CSFs)

$$\mathbf{\Psi}^\lambda_{SM,m}(\mathbf{r},\sigma) = \xi_\lambda \widehat{A}\big[\langle\sigma|SM,m\rangle \mathbf{\Psi}^0_\lambda(\mathbf{r})\big], \tag{20}$$

where

$$\widehat{A} = \frac{1}{N!} \sum_P (-1)^p \widehat{P} \tag{21}$$

is the antisymmetrizer and

$$\xi_\lambda = \sqrt{N!\,2^{-d}} \tag{22}$$

is the normalization constant. In a more general form, the last equation reads

$$|\lambda; SM, m\rangle = \xi_\lambda \widehat{A}\big[|\lambda\rangle|SM, m\rangle\big], \quad m = 1, 2, \ldots, f(S, s). \tag{23}$$

The number of CSFs corresponding to a given configuration $|\lambda\rangle$ is equal to $f(S, s)$ rather than $f(S, N)$. This is because the antisymmetry requirement restricts the spin coupling schemes in this part of $\langle\sigma|SM, m\rangle$ which corresponds to a double in Ψ^0_λ. The spins of those electron pairs that correspond to doubles must be coupled in $\langle\sigma|SM, m\rangle$ to two-electron singlets. Therefore the N-electron spin function $\langle\sigma_1, \sigma_2, \ldots, \sigma_N|SM, m\rangle$ consists of the s-electron spin function $\langle\sigma_1, \sigma_2, \ldots, \sigma_s|SM, m\rangle$, $s = 1, 2, \ldots, f$, multiplied by a product of d singlet-coupled pairs. Though the coupling of the first s spins may be, in principle, arbitrary, we assume that they are coupled according to the Yamanouchi–Kotani scheme [35,50]. In this case the spin space may be described by the Van Vleck branching diagram or, more precisely, by the reversed branching diagram [9,10].

Parallel to the permutation operators $\widehat{P}$ acting on the coordinates of electrons, we define operators $\overline{P}$ acting on the orbital indices. The $\widehat{P}$ and $\overline{P}$ operators, when acting on Ψ^0_λ, are connected by the relation $\overline{P} = \widehat{P}^{-1}$. We denote (st) for a transposition of the indices λ_s and λ_t, and I for the unit operator. The subgroup of $\mathcal{S}_N$, for which Ψ^0_λ is invariant, is denoted Π_λ. It consists of transpositions within doubles and its order is 2^d. Permutations of this subgroup acting on a spin function $|SM, m\rangle$ either change its sign (if the permutation is odd) or leave it invariant (in the even case). Therefore, all permutations belonging to the $\widehat{P}\Pi_\lambda$ coset of $\mathcal{S}_N$ give identical contributions to the CSF.

All CSFs that can be constructed from a given set of orbitals form an orthonormal basis in the FCI space. The dimension of this space is given by the Weyl–Paldus dimension formula [47]

$$D(N, K, S) = \frac{2S+1}{K+1}\binom{K+1}{N/2-S}\binom{K+1}{N/2+S+1}. \tag{24}$$

Model spaces in which the basis vectors are labelled by sequences of either orbital or spin-orbital occupation numbers may be conveniently represented in a graphical way [8]. The model space is described by a graph composed of a network of paths. Each of the paths describes one N-electron basis function. The path is composed of either K or $2K$ arcs, depending upon the mode of the description. The slope of an arc corresponds to the appropriate occupation number. In particular, if the basis in the space is composed of Slater determinants then we have the *two-slope* graphs (since the spin-orbital occupation numbers may be equal to either 0 or 1). In the case of spin-independent Hamiltonians the total spin operators are constants of the motion, so that one can split the model space into spin-adapted FCI subspaces. The basis in each

of these subspaces is composed of spin-adapted combinations of Slater determinants (i.e., of eigenfunctions of the total spin operators $\widehat{S}^2$ and $\widehat{S}_z$). Such spaces may be represented by four-slope graphs (the Shavitt graphs [72]), in which both the orbital and the spin structure of the basis functions are described by each path. This representation of the model spaces is specific for the *unitary group approach* (UGA) to theory of many-electron systems [48]. Alternatively, one may represent the model space as an antisymmetrized direct product of the orbital space and of the spin space, each of them being represented by an independent graph [10]. In the orbital space (spanned by the orbital products $\Psi^0_\lambda(\mathbf{r})$) the occupation numbers of the orbitals in the basis functions may be equal to 0, 1 and 2. Therefore this space may be represented by a *three-slope* orbital graph. The spin space (composed of pure spin functions) is described by a two-slope spin graph also known as the *Van Vleck's branching diagram* [10,50]. This representation of the model spaces is specific for the *symmetric group approach* (SGA) to theory of many-electron systems [10,18].

3. Matrix elements

One of the main objectives of quantum chemistry is to solve for the eigenvalue of the spin-independent Hamiltonian (4) in the FCI space and to evaluate perturbative contributions due to the spin-dependent terms. To this end, the Hamiltonian (4) and its eigenvalue equation are projected onto the FCI space using the appropriate resolution of the identity

$$\widehat{I}_{\mathcal{H}} = \sum_{\lambda} \sum_{m=1}^{f(S,s_\lambda)} |\lambda; SM, m\rangle\langle\lambda; SM, m|. \tag{25}$$

In effect the eigenvalue equation of $\widehat{H}$ transforms into the corresponding algebraic secular problem of the matrix $\mathbf{H}^{(SM)}$ representing $\widehat{H}$ in the SM-adapted FCI space. Its matrix elements are given by

$$H^{\lambda\mu}_{mn} = \big\langle \lambda; SM, m \big| \widehat{H} \big| \mu; SM, n \big\rangle, \tag{26}$$

where, for simplicity, SM indices have been omitted.

Hamiltonians (4) and (1) in the K-orbital Fock space, i.e., also in the FCI space, may be expressed in the second-quantized form

$$\widehat{H} = \sum_{pq}^{2K} a^\dagger_p a_q \big\{ p(1) \big| q(1) \big\} + \frac{1}{2} \sum_{pqrs}^{2K} a^\dagger_p a^\dagger_r a_q a_s \big\{ p(1) q(1) \big| r(2) s(2) \big\}, \tag{27}$$

where p, q, r, s are spin-orbital indices, $a^\dagger_p/a_p$ are the fermion creation/annihilation operators and $\{p|q\}/\{pq|rs\}$ denote the one-/two-electron integrals in the *spin-orbital* basis. If $\widehat{h}_1$ and $\widehat{h}_2$ are spin-independent then one may introduce a spin-traced quantity

$$E_{pq} = a^\dagger_{p\alpha} a_{q\alpha} + a^\dagger_{p\beta} a_{q\beta}, \tag{28}$$

and integrate over the spins. In consequence,

$$\widehat{H} = \sum_{ij}^{K}(i|j)E_{ij} + \frac{1}{2}\sum_{ijkl}^{K}(ij|kl)(E_{ij}E_{kl} - \delta_{jk}E_{il}), \tag{29}$$

where i, j, k, l refer to orbitals and $(i|j)$/$(ij|kl)$ are the one- and two-electron integrals in the *orbital* basis. The operators E_{ij} are spin-independent. They are known as the *unitary group generators* [48], *shift operators* [43], *replacement operators* [10], *excitation operators* [36]. If $i = j$, then E_{jj} is the occupation number operator:

$$E_{jj}|\lambda\rangle = n_j^{\lambda}|\lambda\rangle, \tag{30}$$

where $n_j^{\lambda} = 0, 1, 2$ is the occupation number of the orbital j in λ.

Algorithms for evaluation of the Hamiltonian matrix elements are of basic importance for designing many quantum chemical methods. In SGA these algorithms are very simple for both spin-independent and spin-dependent cases. Let us assume that the operators $\widehat{h}_1$ and $\widehat{h}_2$ in equation (1) depend on both space and spin variables. To simplify the algebra, let both $\widehat{h}_1$ and $\widehat{h}_2$ be products of two scalar operators: one of them spin-independent and the other one depending upon spin only. This formalism, by only minor and rather obvious modification, can be extended to the most important case of scalar products of two vector operators, as it is, for example, in the case of the spin–orbit interaction. Since the Hamiltonian commutes with all permutations, its matrix element, after using equation (23) may be expressed as

$$H'^{\lambda\mu}_{mn} = 2^{-(d_\lambda+d_\mu)/2} \sum_{P}(-1)^p\langle\lambda|\langle SM, m|\widehat{P}\widehat{H}'|S'M', n\rangle|\mu\rangle. \tag{31}$$

It is easy to observe that permutations belonging to the double coset $\Pi_\lambda\widehat{P}\Pi_\mu$ of $\mathcal{S}_N$ give identical contributions to the sum. Therefore the last equation may be simplified to

$$H'^{\lambda\mu}_{mn} = \sum_{q}\alpha^q_{\lambda\mu}(-1)^p\langle\lambda|\langle SM, m|\widehat{P}_q\widehat{H}'|S'M', n\rangle|\mu\rangle, \tag{32}$$

where the sum runs over all distinct double cosets $\Pi_\lambda\widehat{P}_q\Pi_\mu$ and

$$\alpha^q_{\lambda\mu} = 2^{-(d_\lambda+d_\mu)/2}|\Pi_\lambda\widehat{P}_q\Pi_\mu|, \tag{33}$$

with $|\Pi_\lambda\widehat{P}_q\Pi_\mu|$ being the number of elements in the double coset generated by $\widehat{P}_q$. If the Hamiltonian is spin-independent then the integration over the spin and over the orbital variables may be separated and

$$H^{\lambda\mu}_{mn} = \sum_{q}\alpha^q_{\lambda\mu}U^N_S\left(\widehat{P}_q\right)_{mn}\langle\overline{P}\lambda|\widehat{H}|\mu\rangle\delta(S, S')\delta(M, M'),$$
$$m = 1, 2, \ldots, f(S, s_\lambda),\ n = 1, 2, \ldots, f(S, s_\mu). \tag{34}$$

Substituting the explicit form of the spin-dependent Hamiltonian into the general matrix element expression we get

$$H'^{\lambda\mu}_{mn} = \sum_q (-1)^p \alpha^q_{\lambda\mu} \left[\sum_{i=1}^{N} \langle SM, m | \widehat{P}_q \widehat{h}^\sigma_1(\sigma_i) | S'M', n \rangle \langle \overline{P}_q \lambda | \widehat{h}^u_1(i) | \mu \rangle \right.$$
$$\left. + \sum_{i>j}^{N} \langle SM, m | \widehat{P}_q \widehat{h}^\sigma_2(\sigma_i, \sigma_j) | S'M', n \rangle \langle \overline{P}_q \lambda | \widehat{h}^u_2(i,j) | \mu \rangle \right]. \tag{35}$$

Most of the N-electron integrals over orbital variables vanish due to orthogonality of the orbitals. The remaining ones are easily reduced to one- or two-electron integrals. Finally, in most general terms, the Hamiltonian matrix elements may be expressed as

$$H^{(\lambda\mu)}_{mn} = \sum_{ij}^{K} \Gamma^{ij}_{\lambda m,\mu n}(i|j) + \frac{1}{2} \sum_{ijkl}^{K} \Gamma^{ijkl}_{\lambda m,\mu n}(ij|kl), \tag{36}$$

where $\Gamma^{ij}_{\lambda m,\mu n}$ and $\Gamma^{ijkl}_{\lambda m,\mu n}$ are referred to as the *coupling constants*. The coupling constants have also an alternative meaning: they are, respectively, the first- and the second-order reduced density matrix elements, if $(\lambda m) = (\mu n)$, or reduced transition matrix elements, otherwise. As one can show [10,13,17,18] the coupling constants may be expressed as

$$\Gamma^{ij}_{\lambda m,\mu n} = (-1)^p a_{\lambda\mu} \eta(i,j) \langle SM, m | \widehat{P} h^\sigma_1(\sigma_{j\mu}) | S'M', n \rangle \tag{37}$$

and

$$\Gamma^{ijkl}_{\lambda m,\mu n} = (-1)^p a_{\lambda\mu} \eta(i,j,k,l) \langle SM, m | \widehat{P} h^\sigma_2(\sigma_{j\mu}, \sigma_{l\mu}) | S'M', n \rangle, \tag{38}$$

where $a_{\lambda\mu} = 2^{q/2}$ with $q = 0,1,2,3,4$, $\eta(i,j) = 0,1,2$ and $\eta(i,j,k,l) = 0,1,2,4$, depending upon the occupation numbers of the orbitals involved [10,11]. The coefficients η vanish, unless either $\widehat{P} = \widehat{P}_0$ or $\widehat{P} = \widehat{P}_0(i,k)$, where $\widehat{P}_0$ is the permutation which brings orbitals of λ into maximum coincidence with orbitals of μ (referred to as the *line-up permutation*) and (i,k) denotes a transposition. If the Hamiltonian is spin-independent, i.e., h^σ_1 and h^σ_2 are equal to the unit operators, then

$$\Gamma^{ij}_{\lambda m,\mu n} = (-1)^p a_{\lambda\mu} \eta(i,j) V^N_S(P)_{mn} \delta(S,S') \delta(M,M'), \tag{39}$$

$$\Gamma^{ijkl}_{\lambda m,\mu n} = (-1)^p a_{\lambda\mu}\, \eta(i,j,k,l)\, V^N_S(P)_{mn} \delta(S,S') \delta(M,M'). \tag{40}$$

Complete sets of equations for the coupling constant matrices $\Gamma^{ij}_{\lambda\mu}$ and $\Gamma^{ijkl}_{\lambda\mu}$, including explicit forms of the line-up permutations, have been reported by Duch and Karwowski [10,11]. Analogous expressions derived within the UGA formalism may be found in a paper by Robb and Niazi [62]. The N-electron spin integrals appearing in equations (37) and (38) have been calculated in [19] and [13] and, within the unitary group approach, by Kent and Schlesinger [27]. As we see, within the symmetric-group based formalism, the way transition/density matrix elements (39) and (40) depend upon

the spin-coupling scheme is reflected by the form of the $\mathbf{U}_S^N$ matrices only. Therefore, for given λ, μ and i, j or i, j, k, l, a block of coupling constants corresponding to all values of m and n may be constructed at once. In consequence, matrix elements in SGA may be expressed (and coded) in a very compact way [11]. Besides, the general formulation remains valid for any spin-coupling scheme: changing the spin-coupling corresponds to a similarity transformation performed on the $\mathbf{U}_S^N$ matrices. Several different algorithms of evaluation of matrix elements of the representaion matrices have been designed by many authors [7,35,60,61,67,68,71]. Very good reviews of different approaches have been given recently by Pauncz [50,51].

A classification of different types of matrix elements constitutes one of the most important factors in all implementations. The number of orbitals $|\overline{P}_0\lambda\rangle$ and $|\mu\rangle$ differ by is referred to as *rank* of the pertinent matrix element and denoted R. Since the Hamiltonian contains only one- and two-electron operators, the only non-vanishing matrix elements are those with $R = 0, 1, 2$. If $R = 0$, then $\lambda = \mu$. If $R = 1$, then $\overline{P}_0\lambda$ and μ differ by one orbital. If $R = 2$, there are two mismatching orbitals in each of the products. A detailed analysis [10,16–18,65] leads to matrix element expressions which in cases of both spin-dependent and spin-independent operators are analogous to the Slater–Condon rules for matrix elements between single determinants. To facilitate a further classification of $R = 1$ and $R = 2$ matrix elements, the concept of *configuration-pair diagram* has been introduced [18]. A configuration-pair diagram of configurations λ and μ is defined as follows:

1. Singly occupied orbitals are represented by $+$ and doubly occupied orbitals are represented by a linked pair of circles.
2. The symbols for both configurations are placed in two rows – μ above λ.
3. Lines are drawn between λ and μ, linking equal orbitals together in the shortest possible way.

Let $\overline{P}\Delta^{\lambda\mu}$ be the configuration-pair diagram that is obtained when operating with $\overline{P}$ on the orbital position indices in λ and conserving all connection lines. Then, from the definition of the line-up permutation, $\overline{P}_0\Delta^{\lambda\mu}$ is a configuration-pair diagram in which all connection lines are vertical.

Every $\overline{P}_0$ can be factorized:

$$\overline{P}_0 = \overline{P}_0^{\mathrm{sd}}\overline{P}_0^{\mathrm{s}}\overline{P}_0^{\mathrm{d}}, \tag{41}$$

where $\overline{P}_0^{\mathrm{d}}$ permutes only doubles (pairs of orbitals), $\overline{P}_0^{\mathrm{s}}$ permutes only singles and $\overline{P}_0^{\mathrm{sd}}$ mixes doubles with singles. By definition, $\overline{P}_0^{\mathrm{sd}}$ consist of the least number of transpositions possible. Then, only $\overline{P}_0^{\mathrm{sd}}$ breaks doubles in λ. The further classification of $R = 1$ and $R = 2$ matrix elements will depend therefore on the different $\overline{P}_0^{\mathrm{sd}}$ permutations arising for different configuration-pair diagrams. This motivates the introduction of a reduced configuration-pair diagram $\Delta_{\mathrm{sd}}^{\lambda\mu}$, which is obtained from $\overline{P}_0^{\mathrm{s}}\overline{P}_0^{\mathrm{d}}\Delta^{\lambda\mu}$ by

removing all orbitals with vertical connection lines between two doubles or two singles. Since the order of doubles in μ is irrelevant, one can always set $\overline{P}_0^{\mathrm{d}} = \widehat{I}$. In the case of the diagrams, this corresponds to simply assuming that all doubles in μ have been rearranged in such a way as to match those in λ to the maximum extent. Analyzing how many topologically distinct $\Delta_{\mathrm{sd}}^{\lambda\mu}$ may be constructed, one can perform a classification of $R = 1$ and $R = 2$ matrix elements [13,18]. It appears that there are three classes of $R = 1$ and eleven classes of $R = 2$ matrix elements. Each of these classes has been designated as $K_{m(R)}^{R}$ where $R = 1, 2$, while $m(1) = 1, 2, 3$ and $m(2) = 1, 2, \ldots, 11$. The corresponding $\Delta_{\mathrm{sd}}^{\lambda\mu}$ diagrams and $\overline{P}_0^{\mathrm{sd}}$ permutations are listed in table 1. The class of $R = 0$ matrix elements is designated as K_1^0.

This classification scheme has been originally developed by the present author [18] and then applied in later developments of SGGA [9–11]. On a different ground the same results have also been obtained by Sarma and Rettrup [69].

4. The Heisenberg model

The designing of the group-theory-based algorithms of construction and analysis of the Hamiltonian eigenvalue problem in the FCI space, combined with the development in the computer technology resulted in an unprecedented progress in solving the CI eigenvalue problems. However, though the length of the tractable CI expansions have grown up by several orders of magnitude reaching recently 10^9, only small and medium size molecules may be treated this way with sufficient accuracy. For larger systems using simplified, semiempirical, approaches is necessary. Among them, models based on the zero-differential-overlap (ZDO) approximation belong to the most commonly used. They are particularly useful to describing lattices composed of regularly distributed identical atoms. To this cathegory belong the π-electron systems in unsaturated hydrocarbons as well as the Heisenberg and the Hubbard models in solid state physics. In the case of the π-electron systems of conjugated hydrocarbons one may choose an orbital basis in which all but the Coulomb two-electron integrals may be neglected. This approximation is best fulfilled for symmetrically orthogonalized localized $2p\pi$ orbitals, often referred to as *Löwdin orbitals*. In order to describe the magnetic properties of the molecules, one also has to retain the exchange integrals. The two-electron integrals in the Löwdin basis are then assumed to be given by

$$(ij|kl) = \gamma_{ik}\ \delta_{ij}\delta_{kl} + J_{ij}\ \delta_{jk}\delta_{il}, \tag{42}$$

where $\gamma_{ik} = (ii|kk)$ are the Coulomb integrals and $J_{ij} = (ij|ji)$ are the exchange parameters. Substituting equation (42) into equation (29) gives the semiempirical Hamiltonian

$$\widehat{H} = \sum_{i\leqslant j}^{K}(\beta_{ij}E_{ij} + \gamma_{ij}E_{ii}E_{jj} - J_{ij}E_{ji}E_{ij}), \tag{43}$$

Table 1
Classification of the configuration-pairs leading to non-vanishing off-diagonal blocks of CI matrix elements.

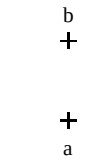
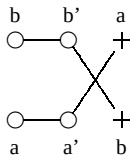
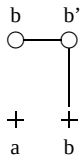
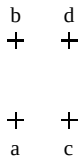
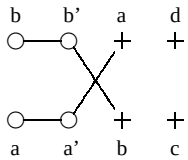
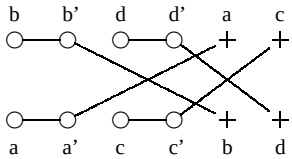
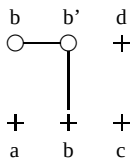
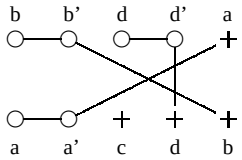
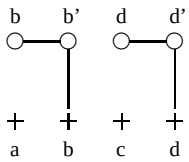
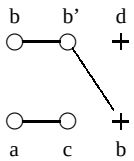
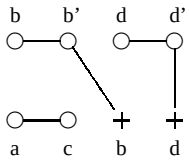
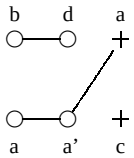
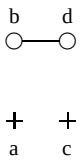
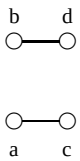
Class	$\Delta_{\mathrm{sd}}^{\lambda\mu}$	$\overline{P}_0^{\mathrm{sd}}$
K_1^1		$\widehat{I}$
K_2^1		$\left(\overline{a}'_\lambda\ \overline{b}_\lambda\right)$
K_3^1		$\widehat{I}$
K_1^2		$\widehat{I}$
K_2^2		$\left(\overline{a}'_\lambda\ \overline{b}_\lambda\right)$
K_3^2		$\left(\overline{a}'_\lambda\ \overline{b}_\lambda\right)\left(\overline{c}'_\lambda\ \overline{d}_\lambda\right)$
K_4^2		$\widehat{I}$

Table 1
(Continued.)

Class	$\Delta_{\mathrm{sd}}^{\lambda\mu}$	$\overline{P}_0^{\mathrm{sd}}$
K_5^2		$\left(\overline{a}'_\lambda\ \overline{b}_\lambda\right)$
K_6^2		$\widehat{I}$
K_7^2		$\left(\overline{c}_\lambda\ \overline{b}_\lambda\right)$
K_8^2		$\left(\overline{c}_\lambda\ \overline{b}_\lambda\right)$
K_9^2		$\left(\overline{a}'_\lambda\ \overline{c}_\lambda\right)$
K_{10}^2		$\widehat{I}$
K_{11}^2		$\widehat{I}$

where $\beta_{ij} = (i|j)$. The Löwdin orbitals are localized on individual atoms. Therefore each orbital product $|\lambda\rangle$ corresponds to a specific distribution of electrons over the orbitals and may be interpreted as a set of $f(S,s)$ valence-bond-type structures. The structures are purely covalent if all the orbital occupation numbers are equal to 1. If some of the occupation numbers are 2 or 0, we have ionic structures with the degree of ionicity equal to the number of the doubly occupied orbitals. This model is frequently referred to as a semi-empirical orthogonal valence bond (VB) method [58].

Matrix elements of Hamiltonian (43) may easily be obtained using the general formalism of SGA [21,22,24]. Due to orthogonality of the orbitals, the matrix elements $H^{\lambda\mu}_{mn} = \langle\lambda; SM, m|\widehat{H}|\mu; SM, n\rangle$ vanish, unless either $\lambda = \mu$ or λ and μ differ by one orbital. In the case of $\lambda = \mu$ we have

$$H^{\lambda\lambda}_{mn} = \delta_{mn} \sum_{i}^{K} \left\{ \beta_{ii} n_i + \binom{n_i}{2} \gamma_{ii} \right\} + \sum_{i \leqslant j}^{K} \left\{ \gamma_{ij} n_i n_j \delta_{mn} + J_{ij} \left[U^s_S\big((\widehat{ij})\big) \right]_{mn} \right\}, \tag{44}$$

where $n_i = 0, 1, 2$ is the occupation number of the ith orbital in λ and $(\widehat{ij})$ is a transposition of the appropriate electron coordinates. If λ and μ differ by one orbital, then

$$H^{\lambda\mu}_{mn} = \pm 2^{|s-s'|/4} \beta_{ij} \left[U^N_S \left(\widehat{P_0}\right) \right]^{ss'}_{mn}, \tag{45}$$

where s and s' stand for the number of singly occupied orbitals, respectively, in λ and μ. The symbol $[\mathbf{U^N_S}]^{ss'}$ means that only $f(S,s)$ rows and $f(S,s')$ columns should be taken from the representation matrix $\mathbf{U^N_S}$. Usually, β_{ik}, γ_{ik} and J_{ij} are treated as empirical parameters. Their fitted values may differ considerably from the ones computed using some analytical potentials and orbitals. Symmetry conditions and further simplifying assumptions (as, e.g., the tight binding approximation) may reduce their number to only a few. In particular, if $J_{ij} = 0$, we obtain the Pariser–Parr–Pople Hamiltonian. The Hubbard Hamiltonian is obtained by setting $\gamma_{ik} = \gamma_{11}\delta_{ik}$ and $J_{ij} = 0$.

The model π-electron Hamiltonian defined in equation (43) reduces to the Heisenberg Hamiltonian if one takes $K = N$ and restricts the N-electron model space to a single orbital configuration in which each of the orbitals appears once [33,58]. Then, in this case the N-particle orbital space is one-dimensional and the N-electron model space contains exclusively the covalent structures. The dimension of the model space is the same as that of the spin space, i.e., it is equal to $f(S,N)$. In the space of covalent structures the VB Hamiltonian may be written as

$$\widehat{H} = \widehat{I} E_0 - \sum_{i<j} \left(\widehat{ij}\right) J_{ij}, \tag{46}$$

where $\widehat{I}$ is the unit operator and

$$E_0 = \sum_i \beta_{ii} + \sum_{i<j} \gamma_{ij}. \tag{47}$$

Matrix elements of the Heisenberg Hamiltonian are given by

$$H_{mn} = E_0 \delta_{mn} + J_{ij} U_S^N \big((\widehat{ij}) \big)_{mn}. \tag{48}$$

The construction of the Heisenberg Hamiltonian matrix within the SGA formalism in the (SM)-adapted model space is very simple – it is merely a linear combination of the representation matrices corresponding to transpositions. In most cases further simplifications are assumed: usually all the nearest-neighbour exchange parameters are equal to each other while the remaining ones are set equal to zero. However, despite this, the problem is far from being trivial. The dimension of the model space grows explosively with N. For $S = 0, 1, 2$ and $N \leqslant 40$ this dimension is given in table 2.

Combining with the Davidson diagonalization routine [4] and the SGA algorithms of constructing the representation matrices, the exact lowest singlet and triplet state energies of the Heisenberg lattices composed of 28 and 30 atoms have recently been obtained [12,14]. However, exact diagonalizations for considerably larger lattices do not seem to be feasible in a foreseable future. Therefore alternative ways of describing spectra have to be developed. One of them, originated in nuclear physics, is the *statistical theory of spectra* [1,44]. In this approach information about spectra is derived from the knowledge of spectral density distribution moments. The moments are defined by traces of Hamiltonian powers. In the case of the Heisenberg Hamiltonian their evaluation is rather simple and the complexity of the approach does not depend upon the size of the lattice.

An arbitrary power of the Heisenberg Hamiltonian may be expressed in terms of products of transpositions. Therefore its spectral density distribution moments may

Table 2
Values of $f(S, N)$ for $S = 0, 1, 2$.

N	Singlets	Triplets	Quintets
2	1	1	0
4	2	3	1
6	5	9	5
8	14	28	20
12	132	297	275
16	1 430	3 432	3 640
20	16 796	41 990	48 450
24	208 012	534 888	653 752
28	2 674 440	7 020 405	8 947 575
32	35 357 670	94 287 120	124 062 000
36	477 638 700	1 289 624 490	1 739 969 550
40	6 564 120 420	17 902 146 600	24 647 883 000

easily be related to the characters of the pertinent representations of the symmetric group. Since

$$\widehat{H}^n = \frac{1}{2^n} \sum_{i_1 \neq j_1}^{N} \sum_{i_2 \neq j_2}^{N} \cdots \sum_{i_n \neq j_n}^{N} J_{i_1 j_1} J_{i_2 j_2} \cdots J_{i_n j_n} \big(\widehat{i_1 j_1}\big) \big(\widehat{i_2 j_2}\big) \cdots \big(\widehat{i_n j_n}\big), \tag{49}$$

we have

$$M_n = \frac{1}{2^n} \sum_{C} \frac{\chi_{[C]}^{[\mathrm{pr}]}}{f(S,N)} \sum_{\{i\}}^{N} \sum_{\{j\}}^{N} J_{i_1 j_1} J_{i_2 j_2} \cdots J_{i_n j_n}, \tag{50}$$

where the first sum is extended over those classes $[C]$ of $\mathcal{S}_{2n} \subset \mathcal{S}_N$, which can be generated by products of n transpositions, $\chi_{[C]}^{[\mathrm{pr}]}$ denote characters of the pertinent representation of $\mathcal{S}_N$ and the sums over $\{i\}$ and $\{j\}$ extend to those combinations of the indices $i_1, i_2, \ldots, i_n$ and $j_1, j_2, \ldots, j_n$, which result in permutations belonging to the appropriate class. In particular [25],

$$M_1 = X_{[2]}^{[\mathrm{pr}]} \frac{1}{2} \sum_{ij}^{N}{}' J_{ij}, \tag{51}$$

$$M_2 = X_{[2^2]}^{[\mathrm{pr}]} \frac{1}{4} \sum_{ijkl}^{N}{}' J_{ij} J_{kl} + X_{[31]}^{[\mathrm{pr}]} \sum_{ijk}^{N}{}' J_{ij} J_{jk} + X_{[1^4]}^{[\mathrm{pr}]} \frac{1}{2} \sum_{ij}^{N}{}' J_{ij}^2, \tag{52}$$

$$\begin{aligned} M_3 = {} & X_{[2^3]}^{[\mathrm{pr}]} \frac{1}{8} \sum_{ijklmn}^{N}{}' J_{ij} J_{kl} J_{mn} + X_{[321]}^{[\mathrm{pr}]} \frac{3}{2} \sum_{ijklm}^{N}{}' J_{ij} J_{jk} J_{lm} \\ & + X_{[21^4]}^{[\mathrm{pr}]} \left[\frac{1}{2} \sum_{ij}^{N}{}' J_{ij}^3 + \sum_{ijk}^{N}{}' \big(3 J_{ij}^2 J_{jk} + J_{ij} J_{jk} J_{ki}\big) + \frac{3}{4} \sum_{ijkl}^{N}{}' J_{ij}^2 J_{kl} \right] \\ & + X_{[41^2]}^{[\mathrm{pr}]} \sum_{ijkl}^{N}{}' (J_{ij} J_{ik} J_{il} + 3 J_{ij} J_{jk} J_{kl}), \end{aligned} \tag{53}$$

where primes mean that all the summation indices are different and

$$X_{[C]}^{[\mathrm{pr}]} = \frac{\chi_{[C]}^{[\mathrm{pr}]}}{f(S,N)} \tag{54}$$

are the normalized irreducible characters, introduced and studied by Klein et al. [33]. A class $[C]$ of $\mathcal{S}_{2n}$ is defined by a partition $t_1, t_2, \ldots, t_q$. In the simplest case, $\chi_{[1^q]}^{[\mathrm{pr}]} = f(S,N)$. In a general case, the characters $\chi_{[C]}^{[\mathrm{pr}]}$ may be expressed using a recently developed method [77].

If all nearest neighbour exchange parameters are equal to $\mathcal{J}$ and all the others vanish, then $J_{ij}/\mathcal{J}$ is the topological matrix of the molecule – its elements are 1 for neighboring atoms and 0 otherwise, and

$$M_n = \mathcal{J}^n \sum_C X^{[\mathrm{pr}]}_{[C]} W_{[C]}. \tag{55}$$

The coefficients $W_{[C]}$ carry all the information about the topology of the molecule. They may be determined from a knowledge of the molecular graph and are referred to as the *topological invariants* of the molecule. In particular, if a denotes the number of bonds in the molecule, b_i – the number of bonds connected to the ith atom,

$$\beta_p = \sum_{i=1}^{N} b_i^p, \qquad \alpha = \sum_{i,j}^{N} b_i b_j J_{ij}/\mathcal{J}$$

and $n(\Delta)$ – the number of three-member cycles formed by the bonds, then [25]

$$\begin{aligned}
W_{[2]} &= 2a,\\
W_{[2^2]} &= a(a+1) - \beta_2,\\
W_{[31]} &= -2a + \beta_2,\\
W_{[1^4]} &= a,\\
W_{[2^3]} &= a(a^2 + 3a + 4) - 3(a+2)\beta_2 + 3\alpha + 2\beta_3 - n(\Delta),\\
W_{[321]} &= -6a(a+2) + 3(a+5)\beta_2 - 6\alpha - 3\beta_3 + 3n(\Delta),\\
W_{[41^2]} &= 10a - 9\beta_2 + 3\alpha + \beta_3 - 3n(\Delta),\\
W_{[21^4]} &= a(3a-2) + n(\Delta).
\end{aligned}$$

The normalized irreducible characters $X^{[\mathrm{pr}]}_{[C]}$ express the way in which these specific features propagate when N and S change. Therefore, they are called *propagation coefficients* [1].

5. Statistical spectroscopy

When information about spectra is derived from a knowledge of traces of powers of the pertinent operator, i.e., from the appropriate moments, then the set of the eigenvalues is considered as if it was a statistical ensemble. The resulting theory is known as the statistical theory of spectra [1,24,44,57]. The statistical theory of spectra is not sensitive to the combinatorial explosion of the full CI approach – the moments may be expressed as explicit closed-form expressions in which the dimension of the model space appears as a parameter. Problems which may be handled by this theory are, in most cases, different from those studied within traditional approaches. In statistical spectroscopy the complete spectra rather than individual eigenvalues are considered. This kind of a global approach frequently reveals some new features of the spectrum. One should also realize that detailed information on individual levels is frequently not

necessary. The statistical description is useful when many eigenvalues are of interest. Spectra of atoms and of nuclei, spectral distributions of eigenvalues of some model Hamiltonians, vibronic spectra of molecules are examples of areas where the statistical spectroscopy is useful.

In spectroscopy most interesting applications are connected with deriving detailed properties of spectra (i.e., the Hamiltonian eigenvalues) from the corresponding moments. This approach may open a way to developing methods of approximating the eigenvalues by quantities whose evaluation is not limited by dimensions of the model spaces. Spectral density distribution moments are independent of a specific representation and can be determined *a priori*, without any N-electron matrix element evaluation [24,46]. The results always correspond to the complete N-electron model space. Since, in this language, no bound property for the approximations to individual eigenvalues exists, the accuracy of the results may be estimated, in principle, by an extrapolation of the cases in which a direct comparison with the exact values is possible. This weakness of the approach is compensated by its generality and insensitivity to the dimension of the problem. In particular, it is expected that it may be very useful in establishing different types of extrapolation and asymptotic formulas for the eigenvalues [25].

A comparison of the real energy levels and those derived from the spectral density distribution moments leads to notions of the secular eigenvalue density and of fluctuations [1,44]. The secular density is defined by a small number of moments. Usually three or four moments are sufficient to obtain a correct secular density [1]. If the secular density is accurate enough, then the fluctuations are small, energy-independent and insensitive to increasing the number of moments used to describe the spectrum. Therefore only several (usually not more than four) moments are of some practical importance.

The moments may be used not only to describing a spectrum. They are invariants of unitary transformations of the basis in the model space. This property has been recently applied to checking correctness of computer-generated matrix representations of Hermitian operators, in particular of CI programs [5,6]. The structure of the equations describing moments may also be useful in detecting symmetries of the model spaces, as, e.g., in establishing conditions under which the particle–hole symmetry is preserved [26]. To this category of applications belong searches for hidden constants of motion [54,63]. Undoubtedly, many other applications are still to be discovered.

For our present purposes it is convenient to express the Hamiltonian (29) in the FCI space in the form

$$\widehat{H} = \frac{1}{2}\sum_{ijkl}^{K} {}^{2}E_{jl}^{ik}[ij|kl], \tag{56}$$

where

$$[ij|kl] = \frac{1}{N-1}\big[(i|j)\delta_{kl} + (k|l)\delta_{ij}\big] + (ij|kl) \tag{57}$$

are the *generalized two-electron integrals* and

$$^2E^{ik}_{jl} = \sum_{\sigma_1\sigma_2} a^\dagger_{i\sigma_1} a^\dagger_{k\sigma_2} a_{l\sigma_2} a_{j\sigma_1} \tag{58}$$

is the second-order reduced density operator [56].

The qth moment of the density distribution of the spectrum of the Hamiltonian $\widehat{H}$ is defined as

$$M_q\big(\widehat{H}\big) = \frac{1}{D}\,\mathrm{Tr}\big(\widehat{H}^q\big), \tag{59}$$

where the trace is taken over the FCI space and D is its dimension. As one can show [56],

$$\mathrm{Tr}\big(\widehat{H}^q\big) = \sum_{\widehat{P}\epsilon\mathcal{S}_{2q}} \big\langle\big\langle\widehat{P}\big\rangle\big\rangle\big\langle\big\{\widehat{P}\big\}\big\rangle, \tag{60}$$

where

$$\big\langle\big\langle\widehat{P}\big\rangle\big\rangle = \mathrm{Tr}\prod_{p=1}^{q} {}^2E^{2p-1\,2p}_{\widetilde{2p-1}\,\widetilde{2p}}, \tag{61}$$

$$\big\langle\big\{\widehat{P}\big\}\big\rangle = \frac{1}{2^q}\sum_{\{i\}}^{K}\sum_{\{k\}}^{K}\prod_{p=1}^{q}\big[i_p\widetilde{i_p}\big|k_p\widetilde{k_p}\big], \tag{62}$$

$\sum_{\{i\}}^{K} \equiv \sum_{i_1,i_2,\ldots,i_q}^{K}$ and the indices with *tilde* are related to the original ones by the appropriate permutation:

$$\big(\widetilde{1},\widetilde{2},\ldots,\widetilde{2q-1},\widetilde{2q}\big) = \widehat{P}(1,2,\ldots,2q-1,2q), \tag{63}$$

$$\big(\widetilde{i_1},\widetilde{k_1},\ldots,\widetilde{i_q},\widetilde{k_q}\big) = \widehat{P}(i_1,k_1,\ldots,i_q,k_q). \tag{64}$$

Equation (60) reveals an important aspect of the statistical theory of spectra. It allows the separation of the dynamical and structural information from that which depends upon the number of particles and upon the spin state of the system.

The *interaction factors* $\langle\{\widehat{P}\}\rangle$ depend on the generalized two-electron integrals only, i.e., on the interaction potentials and on the orbital basis set. They are invariant with respect to unitary transformations of the orbital basis. The interaction factors depend upon a specific model and their classification gives us insight into a basic structure of the spectral density distribution. Recently, a classification scheme of the interaction factors based on diagrammatic many-body perturbation theory techniques has been developed. In particular, it has been shown that the Hugenholtz-type diagrams are most useful in labeling the interaction factors [57]. Another classification of the interaction factors, mostly applied in nuclear physics, has been developed by Nomura [45].

Traces of products of the second-order reduced density operators $\langle\langle \widehat{P} \rangle\rangle$ are referred to as *propagation coefficients*. They may be expressed in a closed form, as polynomials in N and S with the coefficients being rational functions of K [56]. In consequence, within this formalism one can easily see how the moments depend on the number of electrons and on the total spin.

Of special interest is the case of very large model spaces, with $K \gg N$. In this case, referred to as the low-density limit, neither the Pauli principle nor electron correlation effects are essential and all systems exhibit some universal similarities in their spectral properties. In particular, in the case of a system of N noninteracting particles, in the limit of $K \to \infty$, the qth N-particle central moment of the spectral density distribution is given by [1,44]

$$M_q = \sum_{\pi(q)} A(\pi) \binom{N}{p} \prod_r (\mu_r)^{p_r}, \tag{65}$$

where $\pi(q)$ is the partition of q, p is the total number of parts in π, p_r is the number of times that r is found in π, μ_r is the one-particle central moment and

$$A(\pi) = \frac{q!\, p!}{\prod_r p_r!(r!)^{p_r}}. \tag{66}$$

In the case of large N, but $N/K \to 0$, the term with the highest power of N dominates in equation (65). Therefore, since $\mu_1 = 0$, one obtains

$$M_q = \begin{cases} (q-1)!!\,(M_2)^{q/2}, & \text{if } q \text{ is even,} \\ q!!\,\frac{q-1}{6}(M_2)^{q/2}\gamma N^{-1/2}, & \text{if } q \text{ is odd,} \end{cases} \tag{67}$$

where $M_2 = N\mu_2$ and $\gamma = (\mu_2)^{-3/2}\mu_3$ is the skewness of the one-particle distribution. Hence, if N is sufficiently large, the even moments dominate and the distribution becomes Gaussian, independent of μ_r, i.e., independent of the external potential. In the case of particles interacting in an arbitrary way, the asymptotic form of the spectral density distribution is much more complicated [52]. A general discussion of this subject has been given by Nomura [46], where also references to other works on this subject may be found.

6. Concluding remarks

The permutational symmetry belongs to the richest of discrete symmetries. It always appears when one is dealing with a set of identical objects as, for example, with a set of nondistinguishable particles or with a set of identical operators forming a product. In each case exploiting this symmetry leads to simple and compact computational schemes. The symmetric group approach to modelling N-electron systems represented in a FCI space supplies transparent and computationally efficient methods of construction of the wavefunctions, of the evaluation of matrix elements of spin-indepedndent and of spin-dependent operators and, finally, of computing eigenvalues

of the Hamiltonian matrices. The irreducible representation matrices appear as the coupling constants in the expressions for the Hamiltonian matrix elements; construction of the eigenfunctions of the total spin operators is equivalent to the construction of the bases for the irreducible representations; the shapes of spectra may be derived from the knowledge of the irreducible characters; etc. An application of the symmetry of traces of powers of the many-particle operators with respect to permutations of the orbital indices leads to simple classification schemes of the terms appearing in the expressions for spectral density distribution moments. The moments define some global properties of the spectra. A separation of these properties of spectra which are determined by symmetry, in particular by the permutational symmetry, from the ones which are due to specificity of interactions, still remains one of the most interesting questions in theoretical spectroscopy.

There exist many other applications of the symmetric group to developing computational methods of quantum chemistry. A large class of methods originated from the early works of Rumer [66], Reeves [59], Sutcliffe [73], Cooper and McWeeny [3], based on using non-orthogonal spin-paired and spin-projected functions. This approach, most suited to valence-bond-type formulations, has been developed into a powerful theory by Gerrat, Raimondi et al. [2,15,55], Li and Paldus [37–39], Li and Pauncz [40] and by many others. Interesting applications of this approach in theory of the Heisenberg chains are due to Klein and Garcia-Bach [29,30]. Among other applications of the permutational symmetry which have not been discussed in this review, one should mention studies on the invariance of the potential energy surfaces with respect to permutations of the identical atoms.

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