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Spectral density distribution moments of N-electron Hamiltonians in the low-density limit

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Abstract. Previously derived expressions for moments of spectral density distribution of an N-electron Hamiltonian defined in a finite-dimensional model space spanned by a set of spin-adapted antisymmetrized products of orthonormal orbitals (full configuration interaction space) are reduced to the low electron density limit, i.e. to the case when the number of electrons is much smaller than the number of orbitals. The limit of a very large number of electrons is also considered.

1. Introduction

Most theoretical studies on properties of N-electron systems have been concerned with Hamiltonians defined in finite-dimensional model spaces $\mathcal{H}^A$ spanned by antisymmetrized products of spinorbitals (see, for instance, Duch 1986). Usually the spaces are assumed to be spin-adapted, i.e. to belong to specific eigenvalues of the square and of a projection of the total spin operator, $S(S+1)$ and M respectively. These spaces are also known as *full configuration interaction* (FCI) spaces. A large variety of computational methods of quantum chemistry (for reviews see Fraga 1992, Diercksen and Wilson 1992) have been designed to estimate several lowest eigenvalues of the N-electron Hamiltonian matrix defined in this space. Applicability of these methods is, however, either limited to systems of several electrons, or restricted to model studies in relatively small FCI spaces. If K is the number of orbitals, then the dimension of the FCI space is equal to (Paldus 1974)

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

and the FCI problem becomes untractable (even under severe approximations) when K exceeds several hundred.

General information about the global structure of the Hamiltonian spectra in FCI spaces is supplied by moments of the spectral density distribution. If one is interested in several eigenvalues, the knowledge of the spectral density distribution moments is of a rather limited help (though even then it may be quite useful, cf Ratcliff 1971, Bancewicz and Karwowski 1991, Karwowski *et al* 1996). However, when one is willing to describe the whole spectrum, using the moments is about the only practical approach (Porter 1965, Brody *et al* 1981, French and Kota 1982, Bauche *et al* 1988, 1990, Karazija 1991). The moments form a set of fundamental quantities defining global properties of the spectrum. During

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the last two decades many different algorithms have been derived to evaluate moments and many techniques have been designed in order to obtain information about spectra from the knowledge of specific moments. Reviews of the subject have been given, for instance, by Brody *et al* (1981), Bauche *et al* (1988), Bauche and Bauche-Arnoult (1990), Karazija (1991), Karwowski (1994). Important classical contributions are, among others, due to Ginocchio (1973), Ayik and Ginocchio (1974), French (1973), French *et al* (1978), Mon and French (1975), Chang *et al* 1971, Nomura (1972, 1974, 1985, 1986, 1987, 1988).

The asymptotic case of very large spaces corresponding to $K \gg N$ is of a special interest. Its importance is a consequence of its simplicity. A simple, universal, structure of the spectrum at the limit of large K, provides a rare possibility of giving exact answers to questions concerning properties of spectra of the Hamiltonian matrices in FCI spaces. Let us note however, that we are restricted to discrete sets of orbitals and therefore, even at the limit of $K \to \infty$ these sets are not complete.

Very recently, the *symmetric group approach* (SGA) to the theory of many-electron systems developed by Duch and Karwowski (1985) and the language of the diagrammatic approach to the *many-body perturbation theory* (MBPT) of Paldus and Čižek (1976) have been applied to calculate traces of the number operators (Nomura 1988, Karwowski *et al* 1986, Karwowski and Valdemoro 1988), of the density operators (Kutzelnigg 1985, Paldus and Jeziorski 1988, Planelles *et al* 1990, Planelles and Karwowski 1990, 1992, 1997) and of powers of the Hamiltonian operators (Rajadell *et al* 1993, 1995, Planelles *et al* 1996). All these quantities are closely related to the spectral density moments. In the present paper the $K \gg N$ and $K \gg N \gg 1$ asymptotic behaviour of the spectral density distribution moments is discussed.

2. N-electron Hamiltonians and their moments

The N-electron non-relativistic Hamiltonian may be expressed as a sum of two-electron terms

$$\hat{\mathcal{H}}' = \frac{1}{2}\sum_{i\neq j}^{N} \hat{h}_2'(i,j) \tag{2}$$

where

$$\hat{h}_2'(i,j) = \frac{\hat{h}_1(i)\otimes\hat{\mathcal{I}}(j) + \hat{\mathcal{I}}(i)\otimes\hat{h}_1(j)}{N-1} + \hat{h}_2''(i,j) \tag{3}$$

contains one-electron and two-electron operators, $\hat{h}_1$ and $\hat{h}_2''$ respectively, and $\hat{\mathcal{I}}(i)$ stands for the one-electron unit operator. The Hamiltonian is defined in an infinite-dimensional Hilbert space. It is bounded from below and its spectrum, usually, comprises both continuum and discrete parts. A reasonable approximation to the low-energy part of its discrete spectrum may be given by the spectrum of $\hat{\mathcal{H}}'$ projected onto a properly selected FCI space $\mathcal{H}^A$:

$$\hat{H}' = \hat{P}\hat{\mathcal{H}}'\hat{P} \tag{4}$$

where

$$\hat{P} = \sum_{L\in\mathcal{H}^A}^{D} |L\rangle\langle L| \tag{5}$$

the sum is extended over all orthonormal basis vectors of $\mathcal{H}^A$ and D is given by equation (1). In second-quantization formalism we may express this Hamiltonian as

$$\hat{H}' = \frac{1}{2}\sum_{abcd}^{K} {}^2E_{bd}^{ac}\{ab|cd\}' \tag{6}$$

where ${}^2E_{bd}^{ac}$ is the second-order reduced density operator (2-RDO) and

$$\{ab|cd\}' \equiv \langle a(1)c(2)|\hat{h}_2'(1,2)|b(1)d(2)\rangle \tag{7}$$

are the generalized (i.e. including both one- and two-electron interaction operators) two-electron integrals. The reduced density operators are related to the reduced density matrices: their expectation values in a particular N-electron state are equal to the appropriate elements of the reduced density matrix. Their properties have been discussed, among others, by Kutzelnigg (1985), Planelles *et al* (1990), Planelles and Karwowski (1990).

The average energy $\overline{E}' = \frac{1}{D}\operatorname{Tr}\mathbf{H}'$, where $\mathbf{H}'$ is the matrix representation of $\hat{H}'$, may be expressed in terms of traces of two effective one-electron operators, $\hat{\mathcal{J}}'$ and $\hat{\mathcal{K}}'$, referred to as the generalized Coulomb and the generalized exchange operators, respectively. Their matrix representations are:

$$\mathcal{J}_{ij}' = \frac{1}{K}\sum_{k=1}^{K}\{ij|kk\}' \qquad \mathcal{K}_{ij}' = \frac{1}{K}\sum_{k=1}^{K}\{ik|kj\}' \tag{8}$$

and their average values (calculated over the one-electron orbital space), are equal to

$$\langle\mathcal{J}'\rangle = \frac{1}{K}\sum_{i=1}^{K}\mathcal{J}_{ii}' \qquad \langle\mathcal{K}'\rangle = \frac{1}{K}\sum_{i=1}^{K}\mathcal{K}_{ii}'. \tag{9}$$

Then, according to Karwowski and Bancewicz (1987),

$$\overline{E}' = B_{\mathcal{J}}'\frac{N(N-1)}{2} - B_{\mathcal{K}}'\left[\frac{N(N-4)}{4} + S(S+1)\right] \tag{10}$$

with

$$B_{\mathcal{J}}' = \frac{K}{K^2-1}\left(K\langle\mathcal{J}'\rangle - \langle\mathcal{K}'\rangle\right) \tag{11}$$

$$B_{\mathcal{K}}' = \frac{K}{K^2-1}\left(\langle\mathcal{K}'\rangle - \langle\mathcal{J}'\rangle\right). \tag{12}$$

As one can easily see, for $K \gg 1$, $N \gg 1$ and $N \gg S$ the average energy becomes $\frac{N^2}{2}(\langle\mathcal{J}'\rangle - \frac{1}{2}\langle\mathcal{K}'\rangle)$.

It is convenient to redefine the Hamiltonian matrix by introducing

$$\mathbf{H} = \mathbf{H}' - \overline{E}\mathbf{I} \tag{13}$$

where $\mathbf{I}$ is the unit matrix, so that $\operatorname{Tr}\mathbf{H} = 0$. As one can check, $\mathbf{H}$ is equal to the representative in the FCI space of the following operator:

$$\hat{\mathcal{H}} = \frac{1}{2}\sum_{i\neq j}^{N}\hat{h}_2(i,j) \tag{14}$$

with

$$\hat{h}_2(i,j) = \hat{h}_2'(i,j) - \hat{\mathcal{I}}(i)\otimes\hat{\mathcal{I}}(j)B_{\mathcal{J}}' - (i,\hat{j})B_{\mathcal{K}}' \tag{15}$$

where $\widehat{(i,j)}$ denotes the transposition of the orbital coordinates of two electrons. Alternatively, matrix **H** may be obtained by replacing the generalized two-electron integrals $\{ij|kl\}$ appearing in $\hat{\mathcal{H}}'$ by (Karwowski *et al* 1997):

$$\{ij|kl\} = \{ij|kl\}' - B'_{\mathcal{J}}\,\delta_{ij}\delta_{kl} - B'_{\mathcal{K}}\,\delta_{il}\delta_{jk}. \tag{16}$$

In this paper, quantities defined in terms of $\{ij|kl\}$ integrals determined according to equation (16), are denoted by symbols without primes. Thus, for example, $\mathcal{J}_{ij} = \frac{1}{K}\sum_{k=1}^{K}\{ij|kk\}$, $\mathcal{K}_{ij} = \frac{1}{K}\sum_{k=1}^{K}\{ik|kj\}$ and $\overline{E} = \frac{1}{D}\,\mathrm{Tr}\,\mathbf{H}$. Using this convention leads to some significant simplifications of the formalism, since $\langle\mathcal{J}\rangle = \langle\mathcal{K}\rangle = 0$ and, in consequence, $\overline{E} = 0$. Then, the central moments of **H** are

$$M_n = \frac{1}{D}\,\mathrm{Tr}(\mathbf{H}^n). \tag{17}$$

In what follows we use the integrals defined according to equation (16), unless it is stated otherwise.

The nth power of $\hat{\mathcal{H}}$ may be expressed as a linear combination of two-electron, three-electron, ..., $2n$-electron operators:

$$\hat{\mathcal{H}}^n = \frac{1}{2^n}\sum_{q=2}^{2n}\sum_{i_1\neq i_2\neq\cdots\neq i_q}^{N}\hat{\Omega}_q^{(n)}(i_1, i_2, \ldots, i_q). \tag{18}$$

In particular, for $n = 2$

$$\hat{\Omega}_2^{(2)}(i,j) = 2\hat{h}_2(i,j)^2 \tag{19}$$

$$\hat{\Omega}_3^{(2)}(i,j,k) = 4\hat{\mathcal{S}}\hat{h}_2(i,j)\hat{h}_2(j,k) \tag{20}$$

$$\hat{\Omega}_4^{(2)}(i,j,k,l) = \hat{\mathcal{S}}\hat{h}_2(i,j)\hat{h}_2(k,l) \tag{21}$$

and for $n = 3$

$$\hat{\Omega}_2^{(3)}(i,j) = 4\hat{h}'_2(i,j)^3 \tag{22}$$

$$\hat{\Omega}_3^{(3)}(i,j,k) = \hat{\mathcal{S}}[24\hat{h}'_2(i,j)\hat{h}'_2(j,k)^2 + 8\hat{h}'_2(i,j)\hat{h}'_2(j,k)\hat{h}'_2(k,i)] \tag{23}$$

$$\hat{\Omega}_4^{(3)}(i,j,k,l) = \hat{\mathcal{S}}[8\hat{h}'_2(i,j)\hat{h}'_2(i,k)\hat{h}'_2(i,l) + 24\hat{h}'_2(i,j)\hat{h}'_2(j,k)\hat{h}'_2(k,l) + 6\hat{h}'_2(i,j)\hat{h}'_2(k,l)^2] \tag{24}$$

$$\hat{\Omega}_5^{(3)}(i,j,k,l,m) = 12\hat{\mathcal{S}}\hat{h}'_2(i,j)\hat{h}'_2(j,k)\hat{h}'_2(l,m) \tag{25}$$

$$\hat{\Omega}_6^{(3)}(i,j,k,l,m,n) = \hat{\mathcal{S}}\hat{h}'_2(i,j)\hat{h}'_2(k,l)\hat{h}'_2(m,n) \tag{26}$$

where

$$\hat{\mathcal{S}} = \frac{1}{q!}\sum_{\mathcal{P}\in S_q}\mathcal{P} \tag{27}$$

is the symmetrization operator. In the last equation, S_q stands for the $q!$-element symmetric group and $\mathcal{P}$ is a permutation operator. In a general case, expressing the nth power of $\hat{\mathcal{H}}$ as in equation (18) requires some combinatorics. One should also remember that $\hat{h}_2(i,j)$ does not commute with $\hat{h}_2(i,k)$ if $j \neq k$. However, since we are interested only in traces of the Hamiltonian powers, for simplicity, the products of $\hat{h}'_2$ which differ by a cyclic permutation of the operators (as, for example, $\hat{h}'_2(i,j)\hat{h}'_2(j,k)^2$ and $\hat{h}'_2(j,k)\hat{h}'_2(i,j)\hat{h}'_2(j,k)$) are treated as if they were equal to each other.

The operator $\hat{H}^n$ may be expressed in the K-orbital Fock space in two different ways. The first one, used in our previous studies on the moment evaluation in the FCI space

(Rajadell *et al* 1993, 1995, Planelles *et al* 1996), is obtained by directly taking the nth power of the second-quantized form of $\hat{H}$:

$$\hat{H}^n = \frac{1}{2^n} \sum_{a_1,a_2,\ldots,a_n}^{K} \sum_{b_1,b_2,\ldots,b_n}^{K} \sum_{c_1,c_2,\ldots,c_n}^{K} \sum_{d_1,d_2,\ldots,d_n}^{K} \prod_{i=1}^{n} {}^2E_{b_i d_i}^{a_i c_i} \{a_i b_i | c_i d_i\}. \tag{28}$$

From here, using some theorems concerning traces of products of 2-RDOs in the FCI space (Planelles *et al* 1990, Planelles and Karwowski 1990) and some Wick-theorem related combinatorics (Rajadell *et al* 1993), one may show that

$$M_n = \frac{1}{D} \sum_{\mathcal{P} \in S_{2n}} \langle\langle \mathcal{P} \rangle\rangle \langle\{\mathcal{P}\}\rangle. \tag{29}$$

In this equation

$$\langle\{\mathcal{P}\}\rangle == \frac{1}{2^n} \sum_{a_1 a_2 \ldots a_n}^{K} \sum_{c_1 c_2 \ldots c_n}^{K} \left\{ \begin{matrix} a_1 c_1, a_2 c_2, \ldots, a_n c_n \\ \hat{P}[a_1 c_1, a_2 c_2, \ldots, a_n c_n] \end{matrix} \right\} \tag{30}$$

where

$$\{ a_1 c_1, a_2 c_2, \ldots, a_n c_n b_1 d_1, b_2 d_2, \ldots, b_n d_n \} = \prod_{i=1}^{n} \{a_i b_i | c_i d_i\} \tag{31}$$

describe the dynamics of the system and are referred to as the interaction factors and

$$\langle\langle \mathcal{P} \rangle\rangle = \mathrm{Tr} \left(\begin{matrix} 12, 34, \ldots, 2n-12n \\ \hat{P}[12, 34, \ldots, 2n-12n] \end{matrix} \right) \tag{32}$$

where

$$\left(\begin{matrix} a_1 c_1, a_2 c_2, \ldots, a_n c_n \\ b_1 d_1, b_2 d_2, \ldots, b_n d_n \end{matrix} \right) = \prod_{i=1}^{n} {}^2E_{b_i d_i}^{a_i c_i} \tag{33}$$

describe the dependence of M_n on K, N and S and are known as the propagation coefficients.

The second way of expressing $\hat{H}^n$ in the Fock space, commonly used in the statistical theory of nuclear spectra (Ginocchio 1973, Nomura 1972, 1974, Brody *et al* 1981), consists of two steps. In the first step the Fock-space representation of $\hat{\mathcal{H}}^n$ is constructed:

$$\hat{P}\hat{\mathcal{H}}^n\hat{P} = \frac{1}{2^n} \sum_{q=2}^{2n} \sum_{a_1,\ldots,a_q}^{K} \sum_{b_1,\ldots,b_q}^{K} {}^qE_{b_1 b_2 \cdots b_q}^{a_1 a_2 \cdots a_q} \langle a_1 a_2 \cdots a_q | \hat{\Omega}_q^{(n)} | b_1 b_2 \cdots b_q \rangle \tag{34}$$

where ${}^qE_{b_1 b_2 \cdots b_q}^{a_1 a_2 \cdots a_q}$ is the qth-order reduced density operator (q-RDO) and

$$\langle a_1 \cdots a_q | \hat{\Omega}_q^{(n)} | b_1 \cdots b_q \rangle = \langle a_1(1) \cdots a_q(q) | \hat{\Omega}_q^{(n)}(1, \ldots, q) | b_1(1) \cdots b_q(q) \rangle$$

is the q-electron integral. In the second step, many-electron integrals $\langle a_1 \cdots a_q \ | \hat{\Omega}_q^{(n)} | b_1 \cdots b_q \rangle$ are 'internally projected' onto the Fock space. This projection is equivalent to the conversion of the integrals containing products of $\hat{h}_2$ operators into linear combinations of products of the standard two-electron integrals (defined by equation (16)), using the resolution of the one-electron identity in the K-orbital Fock space:

$$\mathcal{I}(1) = \sum_{i=1}^{K} |a_i(1)\rangle\langle a_i(1)|. \tag{35}$$

For example,

$$\langle a_1a_2|\hat{\Omega}_2^{(2)}|b_1b_2\rangle = \langle a_1a_2|\hat{h}_2(1,2)^2|b_1b_2\rangle$$
$$= \sum_{c_1c_2}^{K}\langle a_1a_2|\hat{h}_2|c_1c_2\rangle\langle c_1c_2|\hat{h}_2|b_1b_2\rangle = \sum_{c_1c_2}^{K}\{a_1c_1|a_2c_2\}\{c_1b_1|c_2b_2\}. \tag{36}$$

Using expression (34) one can demonstrate, in the same way as it has been done by Rajadell *et al* (1993) in the context of equation (28), that

$$M_n = \frac{1}{2^n}\sum_{q=2}^{2n}\sum_{\mathcal{P}\in S_q}\langle\Xi_q^{(n)}(\mathcal{P})\rangle_{\rm Av}\langle\Omega_q^{(n)}(\mathcal{P})\rangle_{\rm Av} \tag{37}$$

where

$$\langle\Xi_q^{(n)}(\mathcal{P})\rangle_{\rm Av} = \frac{K^q}{D}\,{\rm Tr}({}^qE^{12\ldots q}_{\mathcal{P}(12\ldots q)}) \tag{38}$$

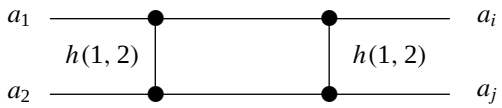
and

$$\langle\Omega_q^{(n)}(\mathcal{P})\rangle_{\rm Av} = \frac{1}{K^q}\sum_{a_1,a_2,\ldots,a_q}^{K}\langle a_1a_2\cdots a_q|\widehat{\Omega}_q^{(n)}|\mathcal{P}(a_1a_2\cdots a_q)\rangle \tag{39}$$

are the average values of the q-RDO and of the q-electron operator $\hat{\Omega}_q^{(n)}$, respectively.

One should stress that equations (29) and (37) are equivalent only when all many-electron integrals appearing in $\langle\Omega_q^{(n)}(\mathcal{P})\rangle_{\rm Av}$ are expressed in terms of the standard two-electron ones, as in equation (36). From a formal point of view, the RHS and the LHS of equation (36) are not the same. Therefore, an integral containing products of $\hat{h}_2$ operators should be interpreted as a shorthand notation for its internally projected counterpart. In particular, $\hat{\mathcal{H}}^n$ may contain some non-integrable singularities. Imposing the inner projection, one may assume that the Hamiltonian and the orbital space are defined in such a way that all the average values defined in equation (39) are finite.

In order to facilitate an easy manipulation with the averages $\langle\Omega_q^{(n)}(\mathcal{P})\rangle_{\rm Av}$ of the q-electron operators containing n-fold products of $\hat{h}_2$, it is convenient to introduce their graphical representation. Then, $\langle\Omega_q^{(n)}(\mathcal{P})\rangle_{\rm Av}$ is represented by a set of q horizontal lines connected by n vertical arcs. Each horizontal line corresponds to an electron and is labelled by the orbital indices of two orbitals which depend upon this electron coordinates: the *bra* index stands to the left of the line and the *ket* one (to the right). An arc which connects the lines corresponding to electrons i and j describes the operator $\hat{h}_2(i,j)$. Then, for example

$\langle\Omega_2^{(2)}(\mathcal{P})\rangle_{\rm Av} \Leftrightarrow$ 

(40)

where

$$\langle\Omega_2^{(2)}(\mathcal{I})\rangle_{\rm Av} = \frac{2}{K^2}\sum_{a_1a_2}^{K}\langle a_1a_2|\hat{h}_2(1,2)^2|a_1a_2\rangle = \frac{2}{K^2}\sum_{a_1a_2a_3a_4}^{K}\langle a_1a_2|\hat{h}_2|a_3a_4\rangle\langle a_3a_4|\hat{h}_2|a_1a_2\rangle$$
$$= \frac{2}{K^2}\sum_{a_1a_2a_3a_4}^{K}\{a_1a_3|a_2a_4\}^2 \tag{41}$$

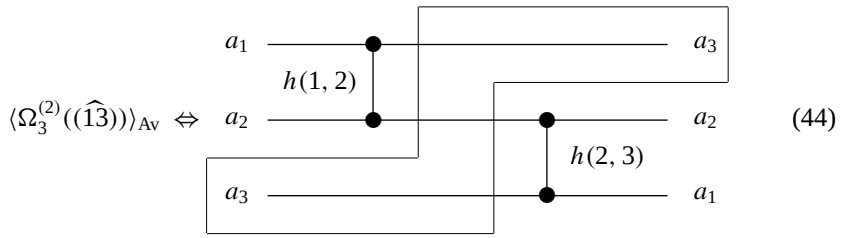
corresponds to $i=1$, $j=2$ and

$$\langle\Omega_2^{(2)}((\hat{12}))\rangle_{\rm Av} = \frac{2}{K^2}\sum_{a_1a_2}^{K}\langle a_1a_2|\hat{h}_2(1,2)^2|a_2a_1\rangle = \frac{2}{K^2}\sum_{a_1a_2a_3a_4}^{K}\{a_1a_3|a_2a_4\}\{a_2a_3|a_1a_4\} \tag{42}$$

corresponds to $i = 2$ and $j = 1$. The transformation

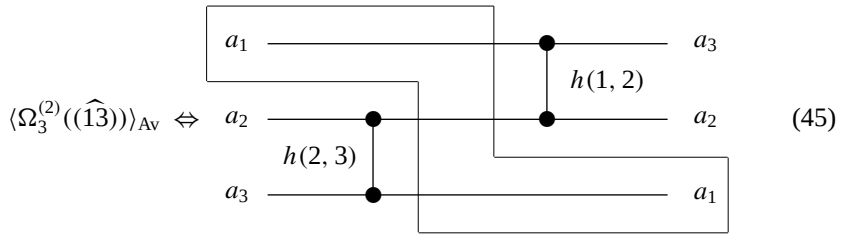
$$\begin{aligned}\langle\Omega_3^{(2)}((\hat{13}))\rangle_{\mathrm{Av}} &= \frac{4}{K^3}\sum_{a_1a_2a_3}^{K}\langle a_1a_2a_3|\hat{h}_2(1,2)\hat{h}_2(2,3)|a_3a_2a_1\rangle \\ &= \frac{4}{K^3}\sum_{a_1a_2a_3a_4}^{K}\langle a_1a_2|\hat{h}_2(1,2)|a_3a_4\rangle\langle a_3a_4|\hat{h}_2(1,2)|a_1a_2\rangle \\ &= \frac{4}{K^3}\sum_{a_1a_2}^{K}\langle a_1a_2|\hat{h}_2(1,2)^2|a_1a_2\rangle = \frac{2}{K}\langle\Omega_2^{(2)}(\mathcal{I})\rangle_{\mathrm{Av}} \end{aligned} \tag{43}$$

is illustrated by the following diagram



(44)

where the frame corresponds to the projector. By removing the framed part of this diagram and linking together the remaining parts of the top and bottom lines into a single top line, we transform diagram (44) into the one presented in equation (40). The operators $\hat{h}(1,2)$ and $\hat{h}(2,3)$ do not commute. However, the trace of a product of operators is invariant with respect to their cyclic permutation. Therefore diagram (44) may be rewitten as



(45)

In a similar way one may show that

$$\langle\Omega_3^{(2)}((1\hat{2}3))\rangle_{\mathrm{Av}} = \langle\Omega_3^{(2)}((1\hat{3}2))\rangle_{\mathrm{Av}} = \frac{2}{K}\langle\Omega_2^{(2)}((\hat{12}))\rangle_{\mathrm{Av}}. \tag{46}$$

Each of these two cases is not symmetric with respect to an interchange of a_1 and a_3 and therefore in order to prove one of them one has to use diagram (44) and in order to prove the other one—diagram (45).

3. The low-density systems

Since only systems with a finite (though large) number of particles are considered here, the conditions $K \gg N$ and $N/K \ll 1$ are equivalent. We are going to investigate the behaviour of the spectral density distribution moments in the case of $K \gg N \gg n$. In this case, referred to as the low-density limit, all N-electron systems possess some common features, to a large extent independent of their specific properties. In particular, some effects

associated with the Pauli principle, as for example, those related to double occupancy of orbitals, are not essential. This may be easily seen by considering a Hamiltonian in an N-electron model space defined as the antisymmetric part of the N-fold Cartesian product of the $2K$-dimensional one-electron spin-orbital space, i.e in a space spanned by all N-electron Slater determinants formed using the set of $2K$ spinorbitals. The dimension of this space is equal to

$$\mathcal{D} = \binom{2K}{N} \Rightarrow \frac{(2K)^N}{N!} \tag{47}$$

where $\Rightarrow$ denotes a transition to the asymptotic form, in which the leading term dependent upon the quantity approaching the limit (K in this case) is retained. The number of determinants in which j orbitals ($j = 1, 2, \ldots, N/2$) are doubly occupied and $(K - j)$ are singly occupied is equal to

$$\mathcal{D}_j = 2^{N-2j}\binom{K-j}{N-2j}\binom{K}{j} \Rightarrow \frac{(2K)^{N-j}}{2^j\, j!(N-2j)!}. \tag{48}$$

If $K/N \to 0$, then

$$\frac{\mathcal{D}_j}{\mathcal{D}} \Rightarrow \frac{1}{(2K)^j}\binom{N}{2j}(2j-1)!! \to \begin{cases} 1 & \text{if } j = 0 \\ 0 & \text{if } j > 0. \end{cases} \tag{49}$$

Hence, in the low-density limit the probability of an orbital being doubly occupied vanishes. However, some of the Pauli-principle-related properties are retained also in the low-density limit. For example, according to equation (10), if $K \gg 1$, $N \gg 1$ and $N \gg S$, then $\overline{E}' \Rightarrow \frac{N^2}{2}(\langle \mathcal{J}' \rangle - \frac{1}{2}\langle \mathcal{K}' \rangle)$. The negative contribution from the exchange operator is a consequence of the antisymmetry of the space (this contribution would be positive in the case of a symmetric, i.e. bosonic, model space).

If the one-particle model is valid, i.e. if the electrons may be considered as non-interacting particles moving in an external potential field then, in the limit $K \gg N$, the nth N-particle central moment of the spectral density distribution is given by (Mon and French 1975, Brody *et al* 1981)

$$M_n = \sum_{\pi_n} \frac{n!\, N!}{(N-p)!} \prod_r \frac{(\mu_r)^{p_r}}{p_r!(r!)^{p_r}} \tag{50}$$

where π_n is the partition of n, p is the total number of parts in π, p_r is the number of times that r is found in π and μ_r is the one-particle central moment. If $K \gg N \gg n$, the term with the highest power of N dominates in equation (50). Therefore, since $\mu_1 = 0$, one obtains

$$M_n = \begin{cases} (n-1)!!(M_2)^{n/2} & \text{if } n \text{ is even} \\ n!!\dfrac{n-1}{6}(M_2)^{n/2}\gamma N^{-1/2} & \text{if } n \text{ is odd} \end{cases} \tag{51}$$

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 (Mon and French 1975, Brody *et al* 1981). This is certainly one of the most remarkable results of the statistical theory of spectra.

In general, the S-dependence of moments and of related quantities is also retained in the low-density limit. In order to express this dependence in a compact way, it is convenient to define a coefficient

$$C_t(\pi_q) = \prod_r [t^r + (1-t)^r]^{p_r} \tag{52}$$

where $t = \frac{x}{N}$ and $x = N/2 + S$ is the numbers of boxes in the first row of the two-row Young diagram labelling the pertinent irreducible representaion of S_N. If the partition contains only one cycle with a length larger than 1, then

$$C_t(1^{q-r}r) \equiv C_t^{(r)} = t^r + (1-t)^r. \tag{53}$$

The coefficient $C_t(\pi_q)$ is a monotonous function of t and varies from 1 for $t = 1$ (i.e. for the high-spin systems) to 2^{p-q} for $t = \frac{1}{2}$, (i.e. for the low-spin systems). Using this notation, the average energy (equation (10)) for $K \gg N \gg 1$ may be expressed as

$$\overline{E} = \frac{N^2}{2}[\langle \mathcal{J}' \rangle - C_t^{(2)} \langle \mathcal{K}' \rangle]. \tag{54}$$

The dimensions of spin-adapted FCI model spaces in the low-density limit depend upon both N and S. Since for $K \gg m$

$$\binom{K}{m} \Rightarrow \frac{K^m}{m!} \tag{55}$$

the asymptotic behaviour of $D(S, N, K)$ may readily be obtained from equation (1) as

$$D(S, N, K) \Rightarrow \frac{f(S, N)}{N!} K^N \tag{56}$$

where

$$f(S, N) = \frac{2S+1}{N+1}\binom{N+1}{N/2-S} \tag{57}$$

is the dimension of the space of N-electron spin functions corresponding to given S and M (see also Nomura 1987 and 1988).

The asymptotic form of the traces of products of the orbital occupation number operators $n_1, n_2, \ldots, n_q$, in the FCI space of $N - 2k$ electrons, $K - k$ orbitals and spin S,

$$W_q(k) = \langle n_1 n_2 \cdots n_q \rangle_{S, N-2k, K-k} \tag{58}$$

may also be easily obtained from the general formula. According to equation (24) of Nomura (1988) or equation (17) of Karwowski and Valdemoro (1988) we have

$$W_q(k) = \sum_{j=0}^{[q/2]} A_j(N-2k, q) \frac{(K-k-q)!}{(K-k-j)!} D(S, N-2k-2j, K-k-j) \tag{59}$$

where

$$A_j(N, q) = (-1)^j \frac{q!(N-2j)!}{j!(q-2j)!(N-q)!}. \tag{60}$$

Equations (55) and (56) yield

$$W_q(0) \Rightarrow K^{N-q} \frac{f(S, N)}{(N-q)!}. \tag{61}$$

It is interesting to observe that the ratio

$$R(S, N, k) = \frac{W_{q-2k}(k)}{W_q(0)} \Rightarrow \frac{f(S, N-2k)}{f(S, N)} \tag{62}$$

approaches a K-independent limit. If $N \gg k$ then, after some simple algebra, we obtain

$$R(S, N, k) \Rightarrow t^k(1-t)^k. \tag{63}$$

In particular, if $t \to \frac{1}{2}$, i.e. for the low-spin systems, $R(S, N, k) \to 2^{-2k}$. For the high-spin systems, if $t \to 1$, we have $R(S, N, k) \to \delta_{k0}$.

Combining equations (38), (55), (56), (61) and remembering that

$$W_q(0) = \mathrm{Tr}({}^qE^{12\ldots q}_{12\ldots q}) \tag{64}$$

we obtain the following asymptotic expression for the S- and N-dependent part of equation (37):

$$\langle \Xi_q^{(n)}(\mathcal{P})\rangle_{\mathrm{Av}} \Rightarrow \frac{N!}{(N-q)!}\frac{\mathrm{Tr}({}^qE^{12\ldots q}_{\mathcal{P}(12\ldots q)})}{\mathrm{Tr}({}^qE^{12\ldots q}_{12\ldots q})}. \tag{65}$$

As shown by Planelles and Karwowski (1997), for $K \gg N \gg q$

$$\frac{\mathrm{Tr}({}^qE^{12\ldots q}_{\mathcal{P}(12\ldots q)})}{\mathrm{Tr}({}^qE^{12\ldots q}_{12\ldots q})} \Rightarrow \varepsilon(\mathcal{P})C_t(\pi_q) \tag{66}$$

where $\varepsilon(\mathcal{P})$ is the parity of $\mathcal{P}$. Therefore, for $K \gg N \gg n$, equations (37) and (65) yield

$$M_n \Rightarrow 2^{-n}\sum_{q=2}^{2n} N^q \sum_{\pi_q}\varepsilon(\mathcal{P})C_t(\pi_q)\sum_{\mathcal{P}\in\pi_q}\langle\Omega_q^{(n)}(\mathcal{P})\rangle_{\mathrm{Av}}. \tag{67}$$

Equation (67) may be further simplified by introducing a *class operator*

$$\mathcal{Q}(\pi_q) = \sum_{\mathcal{P}\in\pi_q}\mathcal{P}. \tag{68}$$

This operator commutes with all $\mathcal{R} \in S_q$. In effect, evaluation of the average values of $\Omega_q^{(n)}$ may be performed as in the following example. The contribution to equation (67) due to $\widehat{\Omega}_3^{(2)}(\mathcal{P})$ associated with a class of S_q defined by a fixed partition π_3, is given by

$$\begin{aligned}\sum_{\mathcal{P}\in\pi_3}\langle\Omega_3^{(2)}(\mathcal{P})\rangle_{\mathrm{Av}} &= \frac{4}{K^3}\sum_{a_1,a_2,a_3}^{K}\frac{1}{3!}\sum_{\mathcal{R}\in S_3}\sum_{\mathcal{P}\in\pi_3}\langle a_1a_2a_3|[\mathcal{R}\hat{h}_2(1,2)\hat{h}_2(2,3)]|\mathcal{P}(a_1a_2a_3)\rangle \\ &= \frac{4}{K^3}\sum_{a_1,a_2,a_3}^{K}\langle a_1a_2a_3|\hat{h}_2(1,2)\hat{h}_2(2,3)]|\mathcal{Q}(\pi_3)(a_1a_2a_3)\rangle.\end{aligned} \tag{69}$$

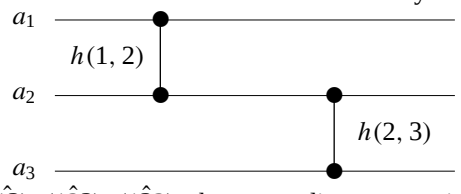
An extension of this example to a general case is straightforward.

4. Low-density, large-N behaviour of the second and of the third moments

Before discussing the general case, let us first illustrate the procedure by considering the low-density and large N limit of the second of the third moments. Apart from its pedagogical values, this special case is of a particular physical importance and deserves a separate treatment.

Two-electron integrals contributing to the second moment have been evaluated in equations (41) and (42). Three-electron contributions are described by the diagram

$\langle\Omega_3^{(2)}(\mathcal{P})\rangle_{\mathrm{Av}} \Leftrightarrow$



. (70)

If $i = 3$ or $k = 1$, i.e. if $\mathcal{P} = (\hat{13})$, $(1\hat{23})$, $(1\hat{32})$, then according to equations (43) and (46), $\langle\Omega_3^{(2)}((\mathcal{P}))\rangle_{\mathrm{Av}}$, vanish. This is because all $\langle\Omega_q^{(n)}(\mathcal{P})\rangle_{\mathrm{Av}}$ are finite and therefore the right-hand sides of equations (43) and (46) approach 0 if $K \to \infty$

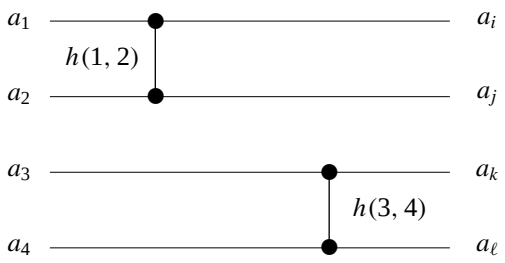
Contributions due to the three remaining permutations of S_3 are finite and may be expressed in terms of the average values of products of the generalized Coulomb and exchange operators. Then, after some algebra,

$$\langle \Omega_3^{(2)}((\hat{\mathcal{I}}))\rangle_{\mathrm{Av}} = 4\,\langle \mathcal{J}^2\rangle \tag{71}$$

$$\langle \Omega_3^{(2)}((\hat{12}))\rangle_{\mathrm{Av}} = \langle \Omega_3^{(2)}((\hat{23}))\rangle_{\mathrm{Av}} = 4\langle \mathcal{K}\mathcal{J}\rangle. \tag{72}$$

Let us note that, due to equation (46), contributions to M_2 proportional to $\langle \mathcal{K}^2\rangle$ vanish in the limit of $K \to \infty$. Contributions to M_2 due to the four-electron operators are described by the diagram

$\langle \Omega_4^{(2)}(\mathcal{P})\rangle_{\mathrm{Av}} \Leftrightarrow$



(73)

and all vanish for $K \to \infty$ because they are either proportional to $\langle \mathcal{J}\rangle$ or $\langle \mathcal{K}\rangle$ (which are equal to 0) or may be contracted to fewer electron terms similarly as in the case of equations (43) and (46).

According to equation (67), contributions to M_2 due to $\langle \Omega_2^{(2)}((\mathcal{P}))\rangle_{\mathrm{Av}}$ are proportional to N^2 while the ones due to $\langle \Omega_3^{(2)}((\mathcal{P}))\rangle_{\mathrm{Av}}$ are proportional to N^3. Therefore, for $N \gg n$ the three-particle terms (equations (71) and (72)) dominate. Using equations (67), (71) and (72), after some simple algebra, we obtain the following asymptotic expression for M_2

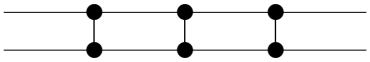
$$M_2 \Rightarrow N^3[\langle \mathcal{J}^2\rangle - 2\langle \mathcal{J}\tilde{\mathcal{K}}\rangle] \tag{74}$$

where

$$\tilde{\mathcal{K}} = C_t^{(2)}\mathcal{K}. \tag{75}$$

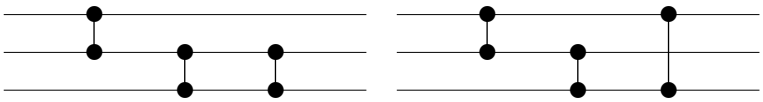
The terms contributing to the third moment in the limit of $K \to \infty$ are described by the following diagrams:

$\langle \Omega_2^{(3)}\rangle_{\mathrm{Av}}$:



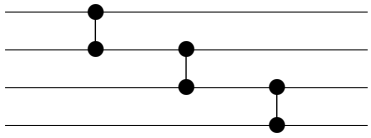
(76)

$\langle \Omega_3^{(3)}\rangle_{\mathrm{Av}}$:



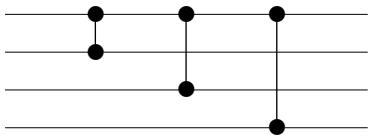
(77)

$\langle \Omega_{4b}^{(3)}\rangle_{\mathrm{Av}} \Leftrightarrow$



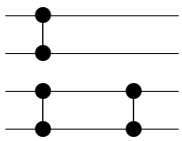
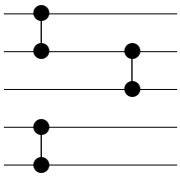
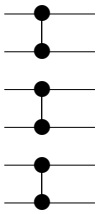
(78)

$\langle \Omega_{4c}^{(3)}\rangle_{\mathrm{Av}} \Leftrightarrow$



(79)

where, for simplicity, all orbital and operator labels have been omitted. The remaining $n = 3$ diagrams, i.e.

$\langle\Omega_{4a}^{(3)}\rangle_{\rm Av} \Leftrightarrow$  $\langle\Omega_{5}^{(3)}\rangle_{\rm Av} \Leftrightarrow$  $\langle\Omega_{6}^{(3)}\rangle_{\rm Av} \Leftrightarrow$  (80)

do not contribute to M_3 if $K \to \infty$, for the same reason as in the case of $\Omega_4^{(2)}$ (diagram (73)).

If $N \gg n$, the dominant contributions are due to $\hat{\Omega}_4^{(3)}$ (similarly as $\hat{\Omega}_3^{(2)}$ dominates in the case of the second moment). The contributions which do not vanish in the limit of $K \to \infty$ are either due to the identity permutation or due to transpositions of the indices corresponding to the pairs of horizontal lines connected by the vertical arcs. Then, in the case of $\hat{\Omega}_{4b}^{(3)}$, represented by the product $\hat{h}_2(1,2)\hat{h}_2(2,3)\hat{h}_2(3,4)$ non-zero contributions are due to $\mathcal{P} = \hat{\mathcal{I}}$, $(\hat{1}2)$, $(\hat{2}3)$, $(\hat{3}4)$, $(\hat{1}2)$, $(\hat{3}4)$. In the case of $\hat{\Omega}_{4c}^{(3)}$, associated with the product $\hat{h}_2(1,2)\hat{h}_2(1,3)\hat{h}_2(1,4)$, the non-zero contributions are due to $\mathcal{P} = \hat{\mathcal{I}}$, $(\hat{1}2)$, $(\hat{1}3)$, $(\hat{1}4)$. In particular,

$$\langle\Omega_{4b}^{(3)}((\hat{\mathcal{I}}))\rangle_{\rm Av} = 24\langle\mathcal{J}\hat{h}_2\mathcal{J}\rangle \tag{81}$$

$$\langle\Omega_{4b}^{(3)}((\hat{1}2))\rangle_{\rm Av} = 24\langle\mathcal{K}\hat{h}_2\mathcal{J}\rangle \tag{82}$$

$$\langle\Omega_{4b}^{(3)}((\hat{3}4))\rangle_{\rm Av} = 24\langle\mathcal{J}\hat{h}_2\mathcal{K}\rangle \tag{83}$$

$$\langle\Omega_{4b}^{(3)}((\hat{1}2)(\hat{3}4))\rangle_{\rm Av} = 24\langle\mathcal{K}\hat{h}_2\mathcal{K}\rangle \tag{84}$$

$$\langle\Omega_{4b}^{(3)}((\hat{2}3))\rangle_{\rm Av} = 24\langle\mathcal{J}\mathcal{K}\mathcal{J}\rangle \tag{85}$$

where

$$\langle\mathcal{J}\hat{h}_2\mathcal{K}\rangle = \frac{1}{K^2}\sum_{a_1a_2}^{K}\langle a_1a_2|\mathcal{J}(1)\hat{h}_2(1,2)\mathcal{K}(2)|a_1a_2\rangle. \tag{86}$$

Similarly,

$$\langle\Omega_{4c}^{(3)}((\hat{\mathcal{I}}))\rangle_{\rm Av} = 8\langle\mathcal{J}^3\rangle \tag{87}$$

$$\langle\Omega_{4c}^{(3)}((\hat{1}2))\rangle_{\rm Av} = \langle\Omega_{4c}^{(3)}((\hat{1}3))\rangle_{\rm Av} = \langle\Omega_{4c}^{(3)}((\hat{1}4))\rangle_{\rm Av} = 8\langle\mathcal{J}\mathcal{K}\mathcal{J}\rangle. \tag{88}$$

Combining these results with equation (67) we obtain the final asymptotic expression for the third moment

$$M_3^b \Rightarrow 3N^4[\langle(\mathcal{J}-\tilde{\mathcal{K}})\hat{h}_2(\mathcal{J}-\tilde{\mathcal{K}})\rangle - \langle\mathcal{J}\tilde{\mathcal{K}}\mathcal{J}\rangle] \tag{89}$$

$$M_3^c \Rightarrow N^4[\langle\mathcal{J}^3\rangle - 3\langle\mathcal{J}\tilde{\mathcal{K}}\mathcal{J}\rangle] \tag{90}$$

and

$$M_3 = M_3^b + M_3^c \tag{91}$$

where the superscripts b and c refer, respectively, to the contributions due to $\langle\Omega_{4b}^{(3)}\rangle_{\rm Av}$ and $\langle\Omega_{4c}^{(3)}\rangle_{\rm Av}$.

5. Low-density, large-N behaviour of higher moments

A procedure similar to the one described in the previous section may be performed for higher moments, except that the number of different terms grows up very rapidly with n (cf Rajadell *et al* 1995, Planelles *et al* 1996). In the low-density limit many terms vanish. In particular, contributions due to all operators of the form

$$\hat{\Omega}(\boldsymbol{a}, \boldsymbol{b}, \ldots, \boldsymbol{c}) = \hat{\Omega}_a(\boldsymbol{a})\hat{\Omega}_b(\boldsymbol{b}) \cdots \hat{\Omega}_c(\boldsymbol{c}) \tag{92}$$

where $\boldsymbol{a}$, $\boldsymbol{b}$,...,$\boldsymbol{c}$ are disjoint sets of variables and vanish unless the permutation $\mathcal{P}$ does not intermix the variables belonging to different sets. If $\hat{\Omega}$ is a product of one-electron operators, then the only permutation which may give a non-zero contribution is the identity. If any of the operators in the RHS to M_n given by $\hat{\Omega}$ vanishes. All these statements may be easily proved in a way similar to that described while deriving expressions for M_2 and M_3, in particular when discussing diagrams (73) and (80).

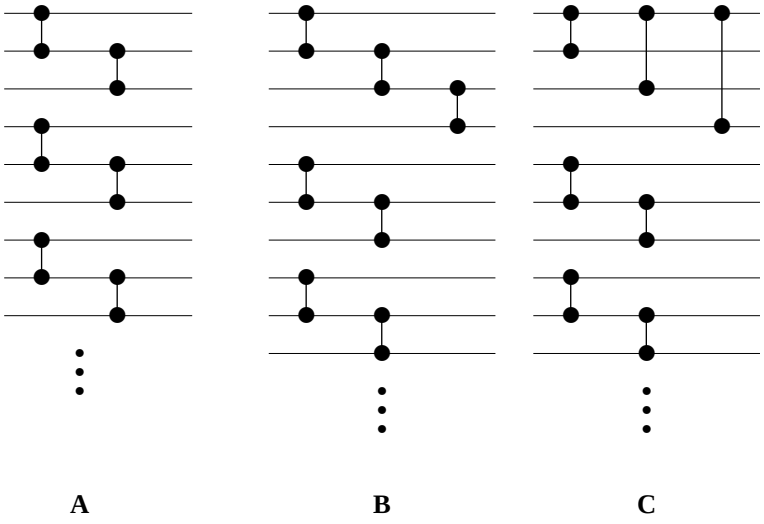


Figure 1. The dominant terms in M_n, when $K \gg N \gg n$, for n even (case A) and for n odd (cases B and C).

According to equation (67), for $N \gg n$, the dominant term in the expression for M_n corresponds to $q_{\max}$, the largest value of q for which $\hat{\Omega}_q^{(n)}$ does not vanish. The value of $q_{\max}$ is equal to the largest number of horizontal lines in the diagrams containing n vertical arcs, none of them being disconnected. The diagrams with $q = q_{\max}$ are shown in figure 1.

The operator for which the average is represented in figure 1, case A, corresponds to the case of even n. Let us set $n = 2k$. Then $q_{\max} = 3k = \frac{3n}{2}$ and the corresponding operator may be expressed as

$$\hat{\Omega}_{3k}^{(2k)}(1, 2, \ldots, 3k) = \frac{(2k)!}{2^k k!}\hat{\Omega}_3^{(2)}(1, 2, 3)\hat{\Omega}_3^{(2)}(4, 5, 6) \cdots \hat{\Omega}_3^{(2)}(3k-2, 3k-1, 3k). \tag{93}$$

It is composed of k disconnected units, each of them described by equation (20) and the corresponding average—by diagram (70).

Cases B and C of figure 1 correspond to odd values of n. Let $n = 2k + 1$. Now $q_{\max} = 3k + 1 = \frac{3n-1}{2}$. The corresponding operator is equal to

$$\hat{\Omega}_{3k+1}^{(2k+1)}(1, 2, \ldots, 3k + 1)$$

$$= \frac{(2k+1)!}{2^{k-1}3!k!}\hat{\Omega}_4^{(3)}(1,2,3,4)\hat{\Omega}_3^{(2)}(5,6,7)\cdots\hat{\Omega}_3^{(2)}(3k-1,3k,3k+1). \tag{94}$$

It is also composed of k units, $k-1$ of them the same as in the previous case. The four-electron operator $\hat{\Omega}_4^{(3)}(1,2,3,4)$ corresponds in case B to diagram (78) and in case C to diagram (79).

Another observation deduced from the analysis performed in the previous section is that the only permutations which may contribute to equation (67) are products of independent transpositions of the orbital indices associated with a single vertical arc. Then, the permutations in question, in cases A, B and C, form the following sets:

$$\mathcal{G}_{2k}^{\mathrm{A}} = (\mathcal{I} + (12) + (23)) \otimes (\mathcal{I} + (45) + (56)) \otimes \cdots (\mathcal{I} + (3k-2, 3k-1) + (3k-1, 3k)) \tag{95}$$

$$\mathcal{G}_{2k+1}^{\mathrm{B}} = (\mathcal{I} + (12) + (23) + (34) + (12)(34)) \otimes (\mathcal{I} + (56) + (67)) \otimes \cdots (\mathcal{I} + (3k-1, 3k) + (3k, 3k+1)) \tag{96}$$

$$\mathcal{G}_{2k+1}^{\mathrm{C}} = (\mathcal{I} + (12) + (13) + (14)) \otimes (\mathcal{I} + (56) + (67)) \otimes \cdots (\mathcal{I} + (3k-1, 3k) + (3k, 3k+1)). \tag{97}$$

The classes of S_q we have to consider are $[1^q]$, $[1^{q-2}2]$, $[1^{q-4}2^2], \ldots, [1^{q-2m}2^m]$, where $m = \frac{n}{2}$ in case A, $m = \frac{n+1}{2}$ in case B and $m = \frac{n-1}{2}$ in case C.

Substituting the above results into equation (67), and after some algebra, we obtain

$$M_{2k} \Rightarrow (2k-1)!![N^3(\langle\mathcal{J}^2\rangle - 2\langle\mathcal{J}\tilde{\mathcal{K}}\rangle)]^k \tag{98}$$

or more briefly:

$$M_{2k}^A = (2k-1)!!{M_2}^k. \tag{99}$$

Similarly,

$$M_{2k+1} = \frac{k}{3}(2k+1)!!M_3{M_2}^{k-1}. \tag{100}$$

As we can see, also in the case of interacting electrons, the energy level density distribution, in the limit, becomes Gaussian. Indeed, $\frac{M_n}{N^{3n/2}}$ is N-independent when n is even and it is proportional to $N^{-1/2}$ if n is odd. Therefore, for $N \gg n$ the even moments dominate. Besides, the relations between the even moments are the same as in the case of the Gaussian distribution.

6. Concluding remarks

The study on the low-density limit of the spectral density distribution moments has given a deeper insight into the structure of the moment-based formalism. The results show that, in fact, only the second and third moments determine the asymptotic behaviour of the distribution. This demonstrates a simple and universal character of N-electron-system spectra in the low-density limit when the number of electrons is large and the basic assumption of this model, i.e. an essentially discrete character of the spectrum, is fulfilled. This applies, for example, to the spacially confined systems.

The one-electron contributions do not appear in our final formulae. They are hidden in the generalized two-electron integrals (equation (16)) but can easily be recovered explicitly. It is worth mentioning, that under assumption that $\mu_1 = 0$, the non-vanishing one-electron contributions are only due to $\langle\mathcal{J}^2\rangle$ and $\langle\mathcal{J}^3\rangle$.

Another interesting observation is the S-dependence of the asymptotic distribution of the spectral density. In the limit of $K \gg N \gg n$ this dependence is very simple: all generalized exchange operators are multiplied by

$$C_t^{(2)} = \frac{1}{4}\left(1 + \frac{4S^2}{N^2}\right). \tag{101}$$

The value of this coefficient varies from $\frac{1}{4}$ for $S = 0$ to $\frac{1}{2}$ for $S = \frac{N}{2}$. Then, the spin effects may effectively enhance the influence of exchange by a factor of 2.

Acknowledgments

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