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The first two moments of energy level distributions in N -electron spin-adapted model spaces

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Abstract. Formulae are derived for the average value and for the dispersion of the spectrum of an electronic Hamiltonian in a finite-dimensional, antisymmetric and spin-adapted space. Both the moments are expressed in terms of the corresponding two-electron quantities. The derivation is based on the theory of spin-adapted reduced Hamiltonians.

1. Introduction

The problem of distribution of eigenvalues of a Hamiltonian is almost as old as quantum mechanics. The early works by Bethe (1936) and by van Lier and Uhlenbeck (1937) were directed towards understanding some general regularities in the structure of N -particle system spectra. Further development of the theory was mainly concerned with applications in nuclear physics. However, many interesting results, valid for any N -particle system, were obtained. An excellent review containing an extensive list of references was recently published by Brody *et al* (1981). Any reader interested in the wide background of the subject should refer to this review.

An interest in an implementation of the statistical approach in the theory of N -electron systems, particularly in the theory of atomic spectra, inspired, at least partly, most of the early works in this field. However, a study on the transition atom spectra by Rosenzweig and Porter (1960) was, to our knowledge, the first work in which some specific features of spectra of many-electron systems were systematically described and explained in terms of their statistical properties. During the following decade, work on this subject became rather scarce. One should mention here contributions by Moszkowski (1962) and Layzer (1963). More recently, important empirical studies were carried out by Parikh (1978) and by Cowan (1981). The latter two authors have demonstrated that the density distribution of energy levels arising from a given atomic configuration is nearly Gaussian. In a most interesting series of papers by Bauche-Arnoult *et al* (1979, 1982, 1985), formulae for the first two moments of the energy distributions of the levels of an atomic configuration and of the radiative transitions between the levels of two configurations were derived and implemented to interpret several atomic spectra. Excellent agreement between the theoretical and experimental results emphasises the usefulness and importance of this kind of study. Some empirical analyses performed by the present authors (Bancewicz and Karwowski

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1984, 1986) indicate that, within a given atomic configuration, subsets of the energy levels belonging to the same symmetry species (to the same angular momentum) exhibit specific statistical properties. In particular, a hypothesis that the density distribution of all energy levels belonging to a given configuration is Gaussian was rejected by the χ^2 test, while the same hypothesis, when applied to subsets of fixed angular momentum energy levels, was accepted. Therefore an evaluation of statistical moments of the energy level density distributions for a fixed symmetry is a task of some practical interest. Its importance was emphasised by French *et al* (French 1974, Mon and French 1975, French and Kota 1982). In nuclear physics some interesting results were obtained by Nomura (1974, 1985, 1986) but for the case of many-electron systems the corresponding formulae have never been published.

In this paper we derive the formulae for the average value and for the dispersion of the spectrum of the electronic Hamiltonian in a finite-dimensional antisymmetric and spin-adapted space. The results may easily be translated to the language of atomic physics. However they are, in fact, much more general and may be applied to any N -electron system. Both the moments are expressed in terms of the corresponding two-electron quantities. Therefore the expressions are useful in studying the general behaviour of N -electron spectra in terms of the number of particles and of the total spin quantum number. The derivation is based on the theory of spin-adapted reduced Hamiltonians recently developed by Valdemoro (1985) and, in particular, on the results of a recent paper by Karwowski *et al* (1986). The paper is organised as follows. In § 2 some relevant definitions and theorems of the spin-adapted reduced Hamiltonian formalism are collected. Then, in § 3, expressions for the average of a Hamiltonian spectrum in an N -electron spin-adapted space are derived. Finally, the last section is concerned with the dispersion of the spectrum. Recurrent formulae allowing us to evaluate all the traces of the occupation number operators met in expressions for the spectral moments are derived in an appendix.

2. Formulation of the problem

We assume the electronic Hamiltonian H to be determined in an antisymmetric and spin-adapted subspace $\mathcal{H}^A(N, K, S, M)$ of a finite-dimensional Hilbert space. The subspace $\mathcal{H}^A(N, K, S, M)$ is defined as the antisymmetric and spin-adapted part of the N -fold tensorial product of a one-electron space

$$\mathcal{H}^A(N, K, S, M) = (V_{2K}^{\wedge N})_{SM}^A \quad (1)$$

where the superscript A stands for antisymmetric and S, M refer to the eigenvalues of the total spin operators. The one-electron space V_{2K} is spanned by a set of $2K$ spin orbitals and is a product of the K -dimensional orbital space

$$V_K^0 = \{\phi_k\}_{k=1}^K \quad (2)$$

spanned by a set of K orthonormal orbitals ϕ_k and of the two-dimensional spin space. The dimension $D(S, N, K)$ of $\mathcal{H}^A(N, K, S, M)$ is given by the Weyl-Paldus formula (Paldus 1974)

$$D(S, N, K) = \frac{2S+1}{K+1} \binom{K+1}{N/2-S} \binom{K+1}{N/2+S+1}. \quad (3)$$

It is convenient to denote

$$D(i) = D(S, N-2i, K-i) \quad i = 0, 1, 2, \dots \quad (4)$$

and $D = D(0)$. We use symbols Tr and tr to denote, respectively, traces of operators in $\mathcal{H}^A(N, K, S, M)$ and in V_K^0 , i.e.

$$\text{Tr } \Omega = \sum_L^D \langle L | \Omega | L \rangle \tag{5}$$

and

$$\text{tr } \omega = \sum_{k=1}^K \langle \phi_k | \omega | \phi_k \rangle. \tag{6}$$

The electronic Hamiltonian may be expressed in the form (cf Paldus 1976)

$$H = \sum_{ij} (i|j) E_{ij} + \frac{1}{2} \sum_{ijkl} (ij|kl) (E_{ij} E_{kl} - \delta_{jk} E_{il}) \tag{7}$$

where

$$\begin{aligned} (i|j) &= \langle \phi_i(1) | h_1(1) | \phi_j(1) \rangle \\ (ij|kl) &= \langle \phi_i(1) \phi_k(2) | h_2(1, 2) | \phi_j(1) \phi_l(2) \rangle \end{aligned} \tag{8}$$

are one/two-electron integrals,

$$E_{ij} = \sum_{k=1}^N |\phi_i(k)\rangle \langle \phi_j(k)| \tag{9}$$

are replacement operators (Paldus 1976, Duch and Karwowski 1985) and $h_1(1)$, $h_2(1, 2)$ describe, respectively, one- and two-electron interactions. Defining

$$h(1, 2) = (h_1(1) + h_1(2)) / (N - 1) + h_2(1, 2) \tag{10}$$

we can rewrite equation (7) in a more compact form as

$$H = \frac{1}{2} \sum_{ijkl} \{ij|kl\} (E_{ij} E_{kl} - \delta_{jk} E_{il}) \tag{11}$$

where

$$\{ij|kl\} = \langle \phi_i(1) \phi_k(2) | h(1, 2) | \phi_j(1) \phi_l(2) \rangle. \tag{12}$$

Operators E_{ii} , referred to as the orbital occupation number operators, are particularly important in our further applications. One can easily see that

$$E_{ii} |\Lambda\rangle = n_i^\Lambda |\Lambda\rangle \tag{13}$$

where $|\Lambda\rangle$ is a basis vector in \mathcal{H}^A and $n_i^\Lambda = 0, 1, 2$ is the occupation number of ϕ_i in $|\Lambda\rangle$. A matrix representation of the Hamiltonian (11) in $\mathcal{H}^A(N, K, S, M)$ is

$$H_{\Lambda\Pi} = \frac{1}{2} \sum_{ijkl} \{ij|kl\} D_{ik,jl}^{\Lambda\Pi} \tag{14}$$

where

$$D_{ik,jl}^{\Lambda\Pi} = \langle \Lambda | E_{ij} E_{kl} - \delta_{jk} E_{il} | \Pi \rangle \tag{15}$$

is the ik, jl element of the reduced second-order transition (if $\Lambda \neq \Pi$) or density (if $\Lambda = \Pi$) matrix. The basis vectors $|\Lambda\rangle$, $|\Pi\rangle$ are spin-adapted antisymmetrised products of the orthogonal orbitals spanning the one-electron space V_K^0 . Explicit formulae for $D_{ik,jl}^{\Lambda\Pi}$ are given by Duch and Karwowski (1985).

The spin-adapted reduced Hamiltonian is determined in a two-electron space. Its matrix representation is (Valdemoro 1985, Karwowski *et al* 1986)

$$H'_{pr,qs} = \frac{1}{2} \sum_{\Lambda \Pi} H_{\Lambda \Pi} D_{pr,qs}^{\Lambda \Pi} \quad (16)$$

The matrix may be factorised by splitting the two-electron orbital space onto the one corresponding to the symmetric (singlet-coupled) and antisymmetric (triplet-coupled) pairs. The corresponding matrices are denoted H^+ and H^- respectively. They are related to H'

$$\begin{aligned} H'_{pr,qs} &= H'_{pr,qs} \pm H'_{pr,sq} && \text{if } p \neq r \text{ and } q \neq s \\ H'_{pp,qs} &= \sqrt{2} H'_{pp,qs} && \text{if } q \neq s \\ H'_{pp,qq} &= H'_{pp,qq} \end{aligned} \quad (17)$$

and may be expressed in a simple way in terms of the two-electron integrals (12) (Karwowski *et al* 1986)

$$H_{pr,qs}^{\pm} = C(pr,qs) (Q_1^{\pm} \{pq|rs\}^{\pm} + Q_2^{\pm} \{r_s^p|00\}^{\pm} + Q_3^{\pm} \{r_0|0_s^q\}^{\pm} + \delta_{pr,qs}^{\pm} R^{\pm}) \quad (18)$$

where

$$\begin{aligned} \{pq|rs\}^{\pm} &= \{pq|rs\} \pm \{ps|rq\} \\ \{r_s^p|00\}^{\pm} &= \delta_{pq} \mathcal{F}_{rs} + \delta_{rs} \mathcal{F}_{pq} \pm \delta_{ps} \mathcal{F}_{rq} \pm \delta_{rq} \mathcal{F}_{ps} \\ \{r_0|0_s^q\}^{\pm} &= \delta_{pq} \mathcal{H}_{rs} + \delta_{rs} \mathcal{H}_{pq} \pm \delta_{ps} \mathcal{H}_{rq} \pm \delta_{rq} \mathcal{H}_{ps} \\ R^{\pm} &= T_2^{\pm} \text{tr } \mathcal{J} + (T_1^{\pm} - T_2^{\pm}) \text{tr } \mathcal{K} \\ C(pr,qs) &= 2^{-(\delta_{pr} + \delta_{qs})/2} \\ \delta_{pr,qs}^{\pm} &= \delta_{pq} \delta_{rs} \pm \delta_{ps} \delta_{qr} \end{aligned} \quad (19)$$

with

$$\mathcal{F}_{pq} = \sum_{k=1}^K \{pq|kk\} \quad \mathcal{H}_{pq} = \sum_{k=1}^K \{pk|kq\} \quad (20)$$

being, respectively, matrix elements of the 'Coulomb' and 'exchange' operators defined over the entire one-electron space. The constants Q_i^{\pm} , $i = 1, 2, 3$, and T_j^{\pm} , $j = 1, 2$, may be expressed in terms of traces of products of at most four different orbital occupation numbers:

$$\begin{aligned} Q_1^+ &= \frac{1}{4} \text{Tr}\{E_{11}(E_{11}-1)(E_{22}-1)(E_{22}-2)\} \\ Q_2^+ &= \frac{1}{4} \text{Tr}\{E_{11}(E_{11}-1)E_{22}(2-E_{33})\} \\ Q_3^+ &= \frac{1}{4} \text{Tr}\{E_{11}(E_{11}-1)E_{22}(E_{33}-E_{22})\} \\ Q_1^- &= \text{Tr}\{E_{11}(E_{11}-E_{44})E_{22}(E_{22}-E_{33})\} - Q_1^+ \\ Q_2^- &= \text{Tr}\{E_{11}E_{22}E_{33}(E_{11}-E_{44})\} - Q_2^+ \\ Q_3^- &= Q_2^- - Q_3^+ - Q_2^- \\ T_1^+ &= \frac{1}{4} \text{Tr}\{E_{11}(E_{11}-1)E_{22}(E_{22}-1)\} \\ T_2^+ &= \frac{1}{4} \text{Tr}\{E_{11}(E_{11}-1)E_{22}E_{33}\} \\ T_1^- &= 2T_2^+ - T_1^+ \\ T_2^- &= \frac{1}{2} \text{Tr}\{E_{11}E_{22}E_{33}E_{44}\} - T_2^+ \end{aligned} \quad (21)$$

The traces, in turn, are rational functions of N , S and K . For explicit expressions see the appendix.

The first two moments of the Hamiltonian spectrum in $\mathcal{H}^A(N, K, S, M)$, i.e. the average energy $\bar{\mathcal{E}}(N, S)$ and the width or the dispersion of the spectrum $\sigma^2(N, S)$ are defined as

$$\bar{\mathcal{E}}(N, S) = \text{Tr } H(N, S) / D \tag{22}$$

and

$$\sigma^2(N, S) = \text{Tr } H(N, S)^2 / D - \bar{\mathcal{E}}(N, S)^2 \tag{23}$$

where $H(N, S)$ is the Hamiltonian matrix with elements given by (14). Both the moments may be, in principle, evaluated using explicit expressions for $H_{\lambda\lambda}$. However it is much simpler to derive them from H' . Indeed, from (13), (15) and (16) we have

$$\sum_{p,r}^K H'_{pr,pr} = \frac{1}{2} \sum_{\Lambda} H_{\Lambda\Lambda} \langle \Lambda | N(N-1) | \Lambda \rangle = \frac{1}{2} N(N-1) \text{Tr } H(N, S) \tag{24}$$

where we used the identity

$$\sum_{p=1}^K n_p^\lambda = N.$$

In the case of the second moment the relation to H' is even more straightforward since, according to (14) and (16),

$$\text{Tr } H(N, S)^2 = \sum_{pqrs} H'_{pr,qs} \{pq|rs\}. \tag{25}$$

3. The average energy

According to (17), (22) and (24)

$$\bar{\mathcal{E}}(N, S) = \frac{2}{DN(N-1)} \sum_{p=1}^K \left\{ H_{pp,pp}^+ + \frac{1}{2} \sum_{\substack{r=1 \\ (r \neq p)}}^K (H_{pr,pr}^+ + H_{pr,pr}^-) \right\}. \tag{26}$$

Substituting (18)–(21) and making use of the expressions for traces of products of the orbital occupation number operators derived in the appendix, after very simple but rather tedious algebra, we finally arrive at a compact and elegant formula

$$\bar{\mathcal{E}}(N, S) = a^+(N, S) \bar{\mathcal{E}}(2, 0)^N + a^-(N, S) \bar{\mathcal{E}}(2, 1)^N \tag{27}$$

where

$$a^\pm(N, S) = \frac{1}{2} [e^{\mp \frac{1}{2} N} (\frac{1}{2} N \pm 1) \mp S(S+1)] \quad e^+ = 1 \quad e^- = 3 \tag{28}$$

and

$$\bar{\mathcal{E}}(2, s)^N = \frac{1}{K(K+\delta)} \sum_{p,q}^K [\{pp|qq\} + \delta\{pq|qp\}] \tag{29}$$

$$\delta = (-1)^s \quad s = 0, 1.$$

Let us note that the one-electron contribution to (29) depends on N since, according to (10) and (12),

$$\{pq|rs\} = (pq|rs) + [\delta_{pq}(r|s) + \delta_{rs}(p|q)]/(N-1). \quad (30)$$

If the one-electron part is explicitly separated then

$$\bar{\mathcal{E}}(N, S) = \bar{E}_1(N, S) + \bar{E}_2(N, S) \quad (31)$$

where $\bar{E}_1(N, S)$ and $\bar{E}_2(N, S)$ are, respectively, the one- and two-electron parts of the average energy. It is easy to see that

$$\bar{E}_1(N, S) = N\bar{E}_1(1) \quad (32)$$

and

$$\bar{E}_2(N, S) = a^+(N, S)\bar{E}_2(2, 0) + a^-(N, S)\bar{E}_2(2, 1) \quad (33)$$

where

$$\bar{E}_1(1) = \bar{E}_1(1, \frac{1}{2}) = \frac{1}{K} \sum_{p=1}^K (p|p) \quad (34)$$

is the average one-electron energy and

$$\bar{E}_2(2, s) = \frac{1}{K(K+\delta)} \sum_{p,q}^K [(pp|qq) + \delta(pq|qp)] \quad \delta = (-1)^s \quad s = 0, 1 \quad (35)$$

are the average two-electron energies of the singlet- and triplet-coupled systems of two electrons.

It is convenient to define Coulomb and exchange operators averaged over the one-electron space. Their matrix elements are, respectively, given by

$$\mathcal{J}'_{pq} = \frac{1}{K} \sum_{k=1}^K (pq|kk) \quad \mathcal{H}'_{pq} = \frac{1}{K} \sum_{k=1}^K (pk|kq). \quad (36)$$

We assume that the one-electron basis functions are chosen so that \mathcal{J}'_{pq} and \mathcal{H}'_{pq} remain finite when $K \rightarrow \infty$. The two-electron average energy may now be expressed as

$$\bar{E}_2(2, s) = \text{tr}(\mathcal{J}' + \delta\mathcal{H}')/(K + \delta). \quad (37)$$

Let us denote

$$\begin{aligned} \bar{\mathcal{J}}_0 &= \frac{1}{K} \sum_{p=1}^K (pp|pp) \\ \bar{\mathcal{J}}_x &= \frac{1}{K(K-1)} \sum_{p \neq q}^K (pp|qq) \\ \bar{\mathcal{H}}_x &= \frac{1}{K(K-1)} \sum_{p \neq q}^K (pq|qp). \end{aligned} \quad (38)$$

Then, from (31), (32) and (37) we obtain

$$\bar{\mathcal{E}}(2, 0) - \bar{\mathcal{E}}(2, 1) = \bar{E}_2(2, 0) - \bar{E}_2(2, 1) = 2(\bar{\mathcal{J}}_0 - \bar{\mathcal{J}}_x + K\bar{\mathcal{H}}_x)/(K+1) \quad (39)$$

and, since $\bar{\mathcal{J}}_0 > \bar{\mathcal{J}}_x > \bar{\mathcal{H}}_x > 0$, we have

$$\bar{\mathcal{E}}(2, 0) > \bar{\mathcal{E}}(2, 1). \quad (40)$$

For large orbital spaces ($K \rightarrow \infty$),

$$\bar{\mathcal{E}}(2, 0) - \bar{\mathcal{E}}(2, 1) = 2\bar{\mathcal{H}}_x. \quad (41)$$

Let us note that differences between average energies of systems with a fixed number of electrons but with different S values do not depend on N . In particular,

$$\bar{\mathcal{E}}(N, S) - \bar{\mathcal{E}}(N, S+1) = (S+1)(\bar{E}_2(2, 0) - \bar{E}_2(2, 1)) \quad (42)$$

which implies (equation (40)) that $\bar{\mathcal{E}}(N, S) > \bar{\mathcal{E}}(N, S+1)$. Similarly

$$\bar{\mathcal{E}}(N+2, S) - \bar{\mathcal{E}}(N, S) = 2\bar{E}_1(1) + (\frac{1}{2}N+1)\bar{E}_2(2, 0) + \frac{3}{2}N\bar{E}_2(2, 1) \quad (43)$$

i.e. the difference is S -independent and linear in N .

The average energy of an N -electron system, regardless of its spin, is equal to

$$\bar{\mathcal{E}}(N) = \sum_S (2S+1)D(S, N, K) \bar{\mathcal{E}}(N, S) \left(\sum_S (2S+1)D(S, N, K) \right)^{-1}. \quad (44)$$

Making use of (3), (27), (31) and (37) we get the well known formula

$$\bar{\mathcal{E}}(N) = N\bar{E}_1(1) + \binom{N}{2} \bar{E}_2(2) \quad (45)$$

with

$$\bar{E}_2(2) = \text{tr}(2\mathcal{F}' - \mathcal{H}') / (2K - 1). \quad (46)$$

4. The dispersion

A substitution of (17)-(20) into (25) gives

$$\begin{aligned} \text{Tr } H(N, S)^2 &= Q_1^+ \text{tr } H(2, 0)^2 + Q_1^- \text{tr } H(2, 1)^2 + Q_2^+ \text{tr}(\mathcal{F} + \mathcal{H})^2 + Q_2^- \text{tr}(\mathcal{F} - \mathcal{H})^2 \\ &\quad + 2(Q_3^+ - Q_2^+) \text{tr } \mathcal{H}^2 + \frac{1}{2}(R^+ + R^-) \text{tr } \mathcal{F} + \frac{1}{2}(R^+ - R^-) \text{tr } \mathcal{H} \end{aligned} \quad (47)$$

where

$$\text{tr } H(2, s)^2 = \frac{1}{4} \sum_{pqrs}^K [\{pq|rs\} + \delta\{ps|rq\}]^2 \quad \delta = (-1)^s \quad s = 0, 1. \quad (48)$$

Now, using (23), (27) and (30) we get

$$\begin{aligned} \sigma^2(N, S) &= A_2^+ \sigma^2(2, 0)^N + A_2^- \sigma^2(2, 1)^N \\ &\quad + B^+ \sigma^2(\mathcal{F} + \mathcal{H})^N + B^- \sigma^2(\mathcal{F} - \mathcal{H})^N + C^+ \sigma^2(\mathcal{H})^N \end{aligned} \quad (49)$$

where the superscript N means that all one-electron integrals are multiplied by a factor $1/(N-1)$ (according to (30)),

$$\begin{aligned} A_2^\pm &= Q_1^\pm K(K \pm 1) / 2D \\ B^\pm &= Q_2^\pm K / D \\ C^+ &= 2(Q_3^- - Q_2^-) K / D \end{aligned} \quad (50)$$

and

$$\sigma^2(a\mathcal{F} + b\mathcal{H}) = \text{tr}(a\mathcal{F} + b\mathcal{H})^2 / K - [\text{tr}(a\mathcal{F} + b\mathcal{H}) / K]^2. \quad (51)$$

Separating in (49) the dispersion of the one-electron Hamiltonian, $\sigma_1^2(h_1)$, and the covariance between the one- and two-electron parts of the Hamiltonian, $\sigma_{12}(h_1, h_2)$, from the dispersion of the two-electron Hamiltonian $\sigma_2^2(h_2)$, we have

$$\begin{aligned} \sigma^2(N, S) = & A_1 \sigma_1^2(1) + A_2^+ \sigma_2^2(2, 0) + A_2^- \sigma_2^2(2, 1) \\ & + K^2 B^+ \sigma_2^2(\mathcal{F}' + \mathcal{H}') + K^2 B^- \sigma_2^2(\mathcal{F}' - \mathcal{H}') + K^2 C^+ \sigma_2^2(\mathcal{H}') \\ & + G^+ \sigma_{12}[h_1(2\mathcal{F}' - \mathcal{H}')] + G^- \sigma_{12}[h_1(\mathcal{F}' - \mathcal{H}')] \end{aligned} \quad (52)$$

where

$$\begin{aligned} A_1 = & K[(K+2)Q_1^+ + (K-2)Q_1^- + (K+2)^2 Q_2^+ + (K-2)^2 Q_2^- + 8(Q_3^+ - Q_2^+)]/D(N-1)^2 \\ G^+ = & 4K^2(Q_1^+ + KQ_2^+ + 2Q_3^+)/D(N-1) \end{aligned} \quad (53)$$

$$G^- = 2K^2[3Q_1^- - Q_1^- + (K-2)(3Q_2^- - Q_2^-) + 8(Q_3^- - Q_2^-)]/D(N-1)$$

and

$$\begin{aligned} \sigma_1^2(h_1) = & \frac{1}{K} \sum_{p,q}^K (p|q)^2 - \bar{E}_1(1)^2 \\ \sigma_2^2(2, s) = & \frac{1}{2} \sum_{pqrs}^K [(pq|rs) + \delta(ps|rq)]^2 / K(K+\delta) - \bar{E}_2(2, s)^2 \end{aligned} \quad (54)$$

$$\sigma_2^2(a\mathcal{F}' + b\mathcal{H}') = \frac{1}{K} \text{tr}(a\mathcal{F}' + b\mathcal{H}')^2 - [\text{tr}(a\mathcal{F}' + b\mathcal{H}')/K]^2$$

$$\sigma_{12}[h_1(a\mathcal{F}' + b\mathcal{H}')] = \frac{1}{K} \sum_{p,q}^K (p|q)(a\mathcal{F}'_{pq} + b\mathcal{H}'_{pq}) - \bar{E}_1(1) \text{tr}(a\mathcal{F}' + b\mathcal{H}')/K.$$

Equation (52) allows us to study the width of the spectrum as a function of N, S and K . The dispersions at the right-hand side of the equation characterise one- and two-electron systems described in the same orbital space as the N -electron system. Information which depends on the number of particles and on the total spin is transferred by A_1, A_2^\pm, B^\pm, C^+ and G^\pm coefficients. Since

$$\begin{aligned} \frac{D(1)}{D(0)} = & [\frac{1}{2}N(\frac{1}{2}N+1) - S(S+1)]/K(K+1) \\ \frac{D(2)}{D(1)} = & [\frac{1}{2}N(\frac{1}{2}N-1) - S(S+1)]/K(K-1) \end{aligned} \quad (55)$$

and

$$Q_i^\pm/D = W(4)_i^\pm + W(2)_i^\pm D(1)/D(0) + W(0)_i^\pm D(2)/D(0) \quad (56)$$

where $W(k)_i^\pm$ is a polynomial in N of the k th degree (consult the appendix for explicit expressions), the coefficients in (52) are the polynomials of a degree not higher than fourth in N and not higher than second in $S(S+1)$. The corresponding formulae may be derived combining (21), (50), (53), (A8) and (A12). After some rather tedious algebra we get

$$A_1 = 2K[\frac{1}{2}N(K - \frac{1}{2}N)(K+2)/K - S(S+1)]/(K+1)(K-1)$$

$$A_2^+ = a^+(N, S)[(K - \frac{1}{2}N)(K - \frac{1}{2}N + 1) - S(S+1)]/K(K-1)$$

$$\begin{aligned}
B^+ &= 2a^+(N, S)[(K - \frac{1}{2}N)(\frac{1}{2}N - 1)(2K - 1) - S(S + 1)] / (K + 1)K(K - 1)(K - 2) \\
C^+ &= -2a^+(N, S)[6(K - \frac{1}{2}N)(\frac{1}{2}N - 1) - S(S + 1)] / (K + 1)(K - 1)(K - 2) \\
A_2^- &= \{\frac{1}{2}N(K - \frac{1}{2}N)[N(K - \frac{1}{2}N)F(1, 1, 3) - (K + 1)F(1, 4, -6)] \\
&\quad - S(S + 1)[2N(K - \frac{1}{2}N)F(1, 3, -3) - KF(5, -1, -6)] \\
&\quad + 2[S(S + 1)]^2F(1, -3, 3) - K(K - 1)A_2^+ \} / K(K + 1) \\
B^- &= \{N(K - \frac{1}{2}N)(\frac{1}{2}N - 1)[NF(0, 2, -1) - 2F(0, 1, 7)] \\
&\quad - 2S(S + 1)[N^2F(0, 1, 2) - 2NF(0, 4, 3) + 12F(0, 1, 0)] \\
&\quad - [S(S + 1)]^2F(0, 0, 4)\} / (K + 1)(K - 1) - B^+ \\
G^+ &= 8a^+(N, S)K(K - \frac{1}{2}N) / (K + 1)(K - 1) \\
G^- &= -2K(K - N)[4a^+(N, S)(2K - 1) / (K + 1) - N(N - 1)] / (K - 1)(K - 2)
\end{aligned} \tag{57}$$

where

$$F(p, q, r) = (pK^2 + qK + r) / (K - 2)(K - 3). \tag{58}$$

Behaviour of the dispersion in a limit of very large orbital spaces is of a particular interest. Let us assume that $K \gg S$ and $K \gg N$ so that $S/K \approx 0$, $N/K \approx 0$ and $F(p, q, r) \approx p$. Then

$$\begin{aligned}
A_1 &\approx N & A_2^\pm &\approx a^\pm & K^2 B^\pm &\approx 2(N - 2)a^\pm \\
K^2 C^+ &\approx -6(N - 2)a^+ & G^+ &\approx 8a^+ & G^- &\approx 4(a^- - 3a^+)
\end{aligned} \tag{59}$$

and

$$\begin{aligned}
\sigma^2(N, S) &\approx N\sigma_1^2(1) + a^+(N, S)\{\sigma_2^2(2, 0) + 2(N - 2)[\sigma_2^2(\mathcal{F}' + \mathcal{H}') - 3\sigma_2^2(\mathcal{H}')] \\
&\quad + 4\sigma_{12}[h_1(\mathcal{F}' + \mathcal{H}')] \} + a^-(N, S)\{\sigma_2^2(2, 1) + 2(N - 2)\sigma_2^2(\mathcal{F}' - \mathcal{H}') \\
&\quad + 4\sigma_{12}[h_1(\mathcal{F}' - \mathcal{H}')] \}.
\end{aligned} \tag{60}$$

A close similarity between this equation and (27), or rather (31)–(33), for the average energies becomes complete when $\sigma^2(\mathcal{F}') = \sigma^2(\mathcal{H}') = 0$, as it is, for example, in the case of an atomic configuration of equivalent electrons. Indeed, both the operators \mathcal{F}' and \mathcal{H}' are spherically symmetric if the sums in (36) run over all orbitals of the configuration and both \mathcal{F}'_{pq} and \mathcal{H}'_{pq} are then scalar matrices; hence, dispersions of spectra of these matrices vanish. From (60) we can see that while $\sigma^2(N + 2, S)$ is, for $K \gg N$, always greater than $\sigma^2(N, S)$, the relation between $\sigma^2(N, S)$ and $\sigma^2(N, S + 1)$ depends upon relations between different dispersions on the right-hand side of (60).

Now we consider a case when both $K \gg 1$ and $N \gg 1$, so that $S/K \approx 0$ and $S/N \approx 0$. From (52) and (57) we get

$$\begin{aligned}
\sigma^2(N, S) &\approx N(1 - N/2K)\{\frac{1}{8}N(1 - N/2K)[\sigma_2^2(2, 0) + 3\sigma_2^2(2, 1)] \\
&\quad + \sigma_1^2[h_1 + N(2\mathcal{F}' - \mathcal{H}')/2]\}
\end{aligned} \tag{61}$$

i.e. the width of the spectrum is spin-independent and reaches its maximum for $N = K$.

One of the most interesting properties of N -electron spectra is their behaviour with respect to a mutual replacement of the particles and holes[†]. As a result of the

[†] A related subject is also discussed in a recent paper of Nomura (1985).

particle-hole symmetry in atoms, spectra of two complementary atomic configurations are the same. Obviously, a necessary condition for a spectrum to be invariant with respect to the particle-hole exchange is that

$$\sigma^2(N, S) = \sigma^2(2K - N, S). \quad (62)$$

The invariance properties of Q_i^\pm may easily be studied by replacing the operators E_{kk} in (21) by $2 - E_{kk}$. Then one finds that

$$Q_1^\pm(N, S) = Q_1^\pm(2K - N, S) \quad (63)$$

but

$$\begin{aligned} Q_2^+(N, S) &= Q_2^+(2K - N, S) - \frac{1}{2}Y_3(N, S) + \frac{3}{2}Y_2(N, S) - Y_1(N, S) \\ Q_2^-(N, S) &= Q_2^-(2K - N, S) - \frac{7}{2}Y_3(N, S) + \frac{5}{2}Y_2(N, S) \\ &\quad + Y_1(N, S) + 4X_2^{\frac{1}{2}}(N, S) - 4X_1^{\frac{1}{2}}(N, S) \end{aligned} \quad (64)$$

$$Q_3^+(N, S) = Q_3^+(2K - N, S) + Y_3(N, S) - Y_2(N, S) - X_3^{\frac{1}{2}}(N, S) + X_1^{\frac{1}{2}}(N, S)$$

where the symbols Y_r and X_r^j are defined in the appendix (in (A1), (A2), (A9) and (A10)) and, for simplicity, the argument K has been left out. The only combination of Q_2^+ , Q_2^- and Q_3^+ which is invariant is $4Q_3^+ + Q_2^+ + Q_2^-$ and, as one can easily check, relations between \mathcal{J} and \mathcal{K} which would lead to (62) due to the invariance of this combination can never be fulfilled. Therefore the necessary condition for a spectrum to be invariant with respect to the particle-hole replacement (equation (62)) is that $\sigma^2(\mathcal{J}) = \sigma^2(\mathcal{K}) = 0$, as it is in the case of configurations of equivalent electrons in atoms.

As was already mentioned in the introduction, the theory developed in this paper may be useful in studying statistical properties of spectra. The simplest global characteristic of a spectrum is given by its first two moments. In many cases this kind of characteristic is entirely sufficient (see, for example, results of an analysis of atomic spectra by Bauche-Arnoult *et al* 1979, 1982, 1985). The general formulae derived in this paper may be easily applied in theory of atoms—then the two-electron integrals ($pq|rs$) have to be replaced by combinations of radial integrals multiplied by products of appropriate 3- j coefficients. The formulae may also be used to study general properties of spectra of N -electron systems as functions of N and S and to determine their shapes. An extension of the formalism to higher moments seems to be particularly attractive. Since a set of all moments determines the spectrum in a complete way, it may be an alternative way of describing an N -electron system in terms of the two-electron ones. Another application of this formalism—checking the correctness of computer programs—was recently proposed by Diercksen and Karwowski (1987).

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Appendix. Traces of products of the orbital occupation number operators

Let us denote

$$Y_r(S, N, K) = \text{Tr}(E_{11}E_{22} \dots E_{rr})_{SNK} \quad (A1)$$

$$Y_0(S, N, K) = \text{Tr}(I)_{SNK} = D(S, N, K) \quad (A2)$$

where subscripts SNK mean that the trace is taken in $\mathcal{H}^A(N, K, S, M)$. We have the following identities:

$$E_{11} = 1 + E_{11}(E_{11} - 1)/2 - (E_{11} - 1)(E_{11} - 2)/2 \tag{A3}$$

$$\text{Tr}(E_{11}(E_{11} - 1)F^1)_{SNK} = 2 \text{Tr}(F^1)_{S, N-2, K-1} \tag{A4}$$

$$\text{Tr}((E_{11} - 1)(E_{11} - 2)F^1)_{SNK} = 2 \text{Tr}(F^1)_{S, N, K-1} \tag{A5}$$

where F^1 stands for an arbitrary function of the orbital occupation number operators not containing E_{11} . Substituting (A3) into (A1) and using (A4) and (A5) we obtain $Y_r(S, N, K) = Y_{r-1}(S, N, K) + Y_{r-1}(S, N - 2, K - 1) - Y_{r-1}(S, N, K - 1)$. (A6)

Equations (A6) and (A2) combined with the dimension formula (3) determine in a recurrent way traces of products of the orbital occupation number operators. In particular, since

$$D(S, N, K - 1) = D(1) + (1 - N/K)D(0) \tag{A7}$$

we have

$$\begin{aligned} Y_1(S, N, K) &= \frac{N}{K} D(0) \\ Y_2(S, N, K) &= \frac{N(N-1)}{K(K-1)} D(0) - \frac{2}{K-1} D(1) \\ Y_3(S, N, K) &= \frac{N(N-1)(N-2)}{K(K-1)(K-2)} D(0) - \frac{6(N-2)}{(K-1)(K-2)} D(1) \\ Y_4(S, N, K) &= \frac{N(N-1)(N-2)(N-3)}{K(K-1)(K-2)(K-3)} D(0) - \frac{12(N-2)(N-3)}{(K-1)(K-2)(K-3)} D(1) \\ &\quad + \frac{12}{(K-2)(K-3)} D(2). \end{aligned} \tag{A8}$$

A similar procedure may be applied to calculation of the traces of products containing squares of the occupation number operators. Let

$$X_r^0(S, N, K) = Y_r(S, N, K) \tag{A9}$$

and

$$X_r^q(S, N, K) = \text{Tr}(E_{11}^2 E_{22}^2 \dots E_{qq}^2 E_{q+1, q+1} E_{q+2, q+2} \dots E_{rr}). \tag{A10}$$

Using (A4) together with the identity

$$E_{11}^2 = E_{11} + E_{11}(E_{11} - 1)$$

we obtain

$$X_r^q(S, N, K) = X_r^{q-1}(S, N, K) + 2X_{r-1}^{q-1}(S, N - 2, K - 1). \tag{A11}$$

In particular,

$$\begin{aligned} X_1^1(S, N, K) &= Y_1(S, N, K) + 2D(1) \\ X_2^1(S, N, K) &= Y_2(S, N, K) + 2 \frac{N-2}{K-1} D(1) \\ X_3^1(S, N, K) &= X_2^1(S, N, K) + 2 \frac{N-2}{K-1} D(1) + 4D(2) \\ X_3^1(S, N, K) &= Y_3(S, N, K) + 2 \frac{(N-2)(N-3)}{(K-1)(K-2)} D(1) - \frac{4}{K-2} D(2). \end{aligned} \tag{A12}$$

All the traces which are needed for evaluation of the first two moments of the Hamiltonian spectrum are listed in (A8) and (A12). Traces which would appear in expressions for higher moments may easily be derived from (A6) and (A11) and from the identity

$$\langle \Lambda | E_{11}(E_{11} - 1)(E_{11} - 2) | \Lambda \rangle = 0 \quad (\text{A13})$$

being fulfilled for an arbitrary $|\Lambda\rangle$. The last identity allows us to reduce any power of an orbital occupation number operator in a trace expression to a linear combination of the first and second powers only.

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