Moments of energy level distributions in vibrational spectra

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Abstract. Expressions for moments of the spectral density distribution of a system described by a *non-symmetric* N-particle Hamiltonian are derived. In particular, this kind of Hamiltonian may represent N coupled oscillators; then its spectrum models the vibrational spectrum of a molecule. It is assumed that the Hamiltonian is defined in a finite-dimensional space formed by products of orthogonal eigenstates of some one-body Hamiltonians. Possible applications of the formalism are briefly discussed.

1. Introduction

Two essentially different strategies may be applied to study eigenvalue spectra of nuclear, atomic, or molecular Hamiltonians. In the first one, individual eigenvalues are evaluated, usually by diagonalization of a matrix representing the Hamiltonian in a model space. This approach is most useful when one is interested in a few, well characterized energy levels. However, it becomes prohibitively inefficient when the number of levels is very large. In the second strategy, global characteristics of the spectra are derived, usually from a knowledge of the appropriate distribution moments. The set of eigenvalues is here treated as a statistical ensemble. In this case, the larger is the ensemble, the more precise is the treatment. The resulting approach is often referred to as *statistical spectroscopy* (French 1974, French and Kota 1982).

The origin of statistical spectroscopy may be traced back to the early works of Bethe (1936) and van Lier and Uhlenbeck (1937). For several decades it was mainly applied in nuclear physics. Early works in this field have been collected and reviewed by Porter (1965). An excellent review was published in 1981 by Brody *et al*. Among more recent works one should mention contributions by Nomura (1985, 1986, 1987), where further references may be found.

The earliest statistical studies of atomic spectra were performed by Rosenzweig and Porter (1960). Reviews on this subject have recently been published by Bauche *et al* (1988), Bauche and Bauche-Arnoult (1990) and Karazija (1991). Interesting applications of the energy level density distribution moments in the crystal field theory has recently been presented by Yeung and Newman (1985, 1986).

Much less explored, though very interesting, are statistical properties of vibrational spectra of molecules. The area of highly excited energy levels, including transition from regular to chaotic behaviours, energy exchange between coupled vibrational-modes in reaction paths, specific features of the nuclear motions near the avoided or allowed crossing regions of the potential energy hypersurfaces, may all be addressed using the statistical approach. The earliest statistical analyses of molecular vibrational spectra were published only a decade ago by Haller *et al* (1983). Since then, statistical studies of the spectra of coupled oscillators have contributed to understanding relationships between classical chaotic systems and their quantum analogues (Zimmermann *et al* 1987, 1988 and references therein), allowed a determination of the effects of molecular complexity on the structure of vibrational spectra (Cimiraglia *et al* 1988), explored how dynamical symmetries influence spacings between vibrational levels (Benjamin *et al* 1984), just to mention a few directions of this fast developing area.

Ensembles of the vibrational energy levels used in statistical studies may be obtained either from experimental measurements or diagonalizing some model Hamiltonian matrices. This restricts the applicability of the approach. In the first case by limited availability of the experimental data, in the second, by numerical complexity of the problem. In the model Hamiltonian calculations the molecule is usually represented as a set of coupled harmonic or Morse oscillators. Taking several eigenvalues for each local mode (one local mode associated with a bond) one easily arrives at hundreds of thousands of eigenvalues for a molecule.

In this paper another method is advocated. The method is based on analysing theoretically derived distribution moments of the quantities considered. A similar approach has been commonly used in statistical studies of both atomic and nuclear spectra (cf Brody *et al* 1981, French and Kota 1982, Nomura 1985, 1986, Bauche and Bauche-Arnoult 1990). General formulae for moments of spectral density distributions of the nuclear energy levels were derived by Ginocchio (1973). In the case of systems of N electrons coupled to given values of the total spin explicit expressions were given by Karwowski and Bancewicz (1987), Rudzikajte and Karazija (1989) and Karazija (1991). In all these works systems of identical particles, either fermions or bosons, have been considered. Therefore the operators considered were *symmetric* in the coordinates of the particles.

In the present paper expressions for moments of the spectral density distribution of a *non-symmetric* N-particle Hamiltonian containing one- and two-body terms are derived. A Hamiltonian of this form may describe a system of coupled oscillators. Then the one-body operators correspond to individual bonds and the two-body ones to the interactions between them. The interaction terms are defined as bilinear forms of one-body operators. It is assumed that the Hamiltonian is defined in a finite-dimensional model space spanned by a set of orthogonal products of eigenfunctions of the one-body operators. In the final formulae, the N-body moments are expressed as linear combinations of products of the primitive one-body moments.

Among various areas where the moments are useful, one should mention two, being of some spectroscopic importance. First, one can generate individual energy levels from moments of the spectral density distributions. This approach was originally proposed and applied to studying nuclear spectra by Ratcliff (1971). In the case of atoms it has been implemented by Bancewicz and Karwowski (1987, 1991). The second possibility is to generate envelopes of spectra. This approach has been formulated and successfully applied in atomic spectroscopy by Bauche *et al* (1988) and

Bauche-Arnoult and Bauche (1992). Its implementation in the case of molecular bands composed of densely packed vibronic transitions was never done, though would be particularly attractive.

2. The Hamiltonian

Let us consider a system described by a Hamiltonian

$$H = H_0' + H_1' \tag{1}$$

where

$$H_0' = \sum_{k=1}^{N} h_k'(k) \tag{2}$$

represents the one-body part, and

$$H_1' = \sum_{k>l}^{N} [\Lambda_{kl} f_k'(k) f_l'(l) + \Gamma_{kl} g_k'(k) g_l'(l)] \tag{3}$$

describes interactions. It is assumed that the one-body Hamiltonians $\{h_k'\}_{k=1}^{N}$ may all be different. In the interaction terms $\Lambda_{kl} = \Lambda_{lk}$ and $\Gamma_{kl} = \Gamma_{lk}$ are numerical constants while $f_k'(k)$ and $g_k'(k)$ are two different one-body operators. For simplicity we assume that $\Gamma_{kl} = 0$, since generalization of the results to the case of arbitrary Γ_{kl} is rather easy. The Hamiltonian may also be represented in a more compact form:

$$H = \sum_{k \geq l}^{N} \Lambda_{kl} \omega_{kl}'(k, l) \tag{4}$$

where $\Lambda_{kk} \omega_{kk}'(k, k) = h_k'(k)$ and $\omega_{kl}'(k, l) = f_k'(k) f_l'(l)$.

If the one-body Hamiltonians are chosen as

$$h_k'(k) = \frac{p(k)^2}{2m_k} + V_k(k) \tag{5}$$

where m_k is the reduced mass of the bond k, $V(k)$ is the bond potential (as, for example, the harmonic oscillator or the Morse potential) and if $f'(k)/g'(k)$ are coordinate/momentum operators (or their powers), then the total Hamiltonian (1) describes the vibrational structure of a molecule containing N bonds (Cimiraglia *et al* 1988).

We assume that h_k' have finite and discrete spectra, i.e.

$$h_k'|k_p\rangle = \varepsilon_p'^k|k_p\rangle \qquad p = 1, 2, \ldots, d_k \qquad k = 1, 2, \ldots, N \tag{6}$$

with $\langle k_p | k_q \rangle = \delta_{pq}$. If the one-body Hamiltonians have infinite spectra (as, for example, the harmonic oscillators) or contain continuum (as, for example, the Morse oscillators) then h_k' are their projections to appropriate finite–dimensional spaces. If the N-body Hamiltonian is designed to describe a real molecule, the projection is aimed at removing the 'unphysical' part of the spectrum.

The total Hamiltonian is defined in an N-body model space being a direct product of the one-body spaces. The basis vectors of the model space are defined as

$$|L\rangle = \prod_{k=1}^{N} |k_{p(L)}\rangle. \tag{7}$$

Since, for a given k, $p(L) = 1, 2, \ldots, d_k$, there are

$$D = \prod_{k=1}^{N} d_k \tag{8}$$

different vectors $|L\rangle$. Orthonormality of $|k_p\rangle$ implies orthonormality of the vectors $|L\rangle$. Therefore D is the dimension of the N-body space. It is easy to see that vectors $|L\rangle$ are eigenvectors of H_0':

$$H_0'|L\rangle = E_L'|L\rangle \tag{9}$$

where

$$E_L' = \sum_{k=1}^{N} \varepsilon'^{k}_{p(L)}. \tag{10}$$

It is convenient to redefine the one-body operators so that their average values vanish. Let us denote

$$h_k''(k) = h_k'(k) - \bar{h}_k' \tag{11}$$

where

$$\bar{h}_k' = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | h_k' | k_p \rangle \tag{12}$$

is the average value of h_k' in its eigenspace. From (6) we obtain

$$\bar{h}_k' = \frac{1}{d_k} \sum_{p=1}^{d_k} \varepsilon_p'^{k}. \tag{13}$$

Similarly

$$f_k(k) = f_k'(k) - \bar{f}_k', \tag{14}$$

with

$$\bar{f}_k' = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | f_k' | k_p \rangle. \tag{15}$$

Then the total Hamiltonian reads

$$H = \bar{E}' + H_0 + H_1 \tag{16}$$

where

$$\bar{E}' = \bar{H} = \frac{1}{D} \operatorname{Tr} H = \frac{1}{D} \sum_{L} E_L' \tag{17}$$

is the average energy of the system, $\text{Tr } Q = \sum_L \langle L|Q|L \rangle$ denotes a trace in the N-body space

$$H_0 = \sum_{k=1}^{N} h_k(k) \tag{18}$$

with

$$h_k(k) = h_k''(k) + f_k(k) \sum_{l(\neq k)}^{N} \Lambda_{kl} \bar{f}_l^l \tag{19}$$

and

$$H_1 = \sum_{k>1}^{N} \Lambda_{kl} f_k(k) f_l(l). \tag{20}$$

As can be easily seen

$$\bar{H} = \sum_{k=1}^{N} h_k' + \sum_{k>l}^{N} \Lambda_{kl} \bar{f}_k^l \bar{f}_l^l. \tag{21}$$

The spectrum of h'' is shifted relatively to that of h' by a constant value

$$\varepsilon_p''^k = \varepsilon_p'^k - \bar{h}_k' \qquad p = 1, 2, \ldots, d_k \tag{22}$$

and the same applies to the spectra of H and H':

$$E_L = E_L' - \bar{E}' \qquad L = 1, 2, \ldots, D \tag{23}$$

where ε'' and E are, respectively, eigenvalues of h'' and H. The average values of h_k'' and f_k vanish. Therefore also the average values of h_k, H_0 and H_1 are equal to zero. By choosing the origin of the energy scale so that $\bar{E}' = 0$, the spectra of H and H' become identical. Then, using the traceless operators does not lead to any loss of generality, while it substantially simplifies the algebra. Therefore only the traceless operators are considered further in this paper.

3. Formulation of the Problem

The (qr)th moment of the one-body spectral density distribution of $h_k f_k$ is defined as

$$\mu_{qr}(k) = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | h_k^q f_k^r | k_p \rangle. \tag{24}$$

The operators h_k and f_k, in general, do not commute. Therefore there are

$$s = \binom{q+r}{q} = \binom{q+r}{r}$$

different products containing q times h_k and r times f_k. Let $\{u_{qr}\}_{i=1}^s$ denote the set of

one-particle moments corresponding to all these products. The average over this set is denoted

$$\bar{\mu}_{qr}(k) = \frac{1}{s} \sum_{l=1}^{s} \{\mu_{qr}(k)\}_l. \tag{25}$$

Of special importance are the spectral density distribution moments of h_k:

$$\mu_{q0}(k) = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | h_k^q | k_p \rangle. \tag{26}$$

Similarly

$$\mu_{0q}(k) = \frac{1}{d_k} \sum_{p=1}^{d_k} \langle k_p | f_k^q | k_p \rangle. \tag{27}$$

The qth moment of the N-body Hamiltonian is

$$M_q = \frac{1}{D} \text{Tr}(H^q). \tag{28}$$

In particular

$$M_1 = \bar{E}. \tag{29}$$

The density of a discrete spectrum may be exactly represented by a discrete normalized frequency function $\bar{\rho}(E)$. The corresponding moments M_q and the average energy $\bar{E}$ may then be expressed as

$$M_q = \int_{-\infty}^{+\infty} E^q \bar{\rho}(E) \, dE. \tag{30}$$

$$\bar{E} = M_1 = \int_{-\infty}^{+\infty} E \bar{\rho}(E) \, dE. \tag{31}$$

If the distribution moments are known, the discrete frequency function may be approximated by a continuous frequency function $\rho(E)$ chosen so that a given number of the lowest moments calculated with both the functions are the same (for details see Kendall 1943). Therefore calculation of the moments directly, using (24)–(28), allows the evaluation of general properties of the spectrum without the need to determine individual energy levels. As we shall see, the moments may be calculated without any explicit evaluation of the Hamiltonian matrix elements.

4. Moments of spectral density distributions

The qth moment of the Hamiltonian spectral density distribution, under assumption that $\bar{E}=0$, is given by

$$M_q = \frac{1}{D} \sum_L^D \langle L | H_0 + H_1 \rangle^q | L \rangle \tag{32}$$

or equivalently by

$$M_q = M_q^{(0)} + M_q^{(1)} + \sum_{j=1}^{q-1} \sum_{r=1}^{S} \{M_{j,q-j}^{01}\}_r \tag{33}$$

where

$$S = \binom{q}{j} \tag{34}$$

and

$$M_q^{(i)} = \frac{1}{D} \operatorname{Tr}(H_i^q) \qquad i = 0, 1. \tag{35}$$

The terms $M_q^{(0)}$ and $M_q^{(1)}$ represent, respectively, contributions due to the one- and the two-particle operators, while $M_{j,q-j}^{(01)}$ describe the effects of coupling between them. The symbol $\{M_{j,q-j}^{01}\}_{r=1}^{S}$ denotes the set of N-particle moments of all products in which H_0 and H_1 appear, respectively, j and $q-j$ times (cf equation (25)).

If the Hamiltonian is expressed as in (4), then

$$M_q = \sum_{k_1 \geqslant l_1}^{N} \sum_{k_2 \geqslant l_2}^{N} \cdots \sum_{k_q \geqslant l_q}^{N} \left(\prod_{i=1}^{N} \Lambda_{k_i l_i} \right) \frac{1}{D} \sum_L^D \langle L | \prod_{i=1}^{q} \omega_{k_i l_i}(k_i, l_i) | L \rangle \tag{36}$$

where the operators ω (cf (4)) are defined in terms of h and f so that $\bar{\omega}_{kl} = 0$ for all pairs k, l.

In order to obtain general expressions for moments of the spectral density distributions, first a system of non-interacting particles, described by one-body operators H_0, will be considered. Then, the approach will be extended to the general case of interacting particles.

4.1. The one-particle operators

The spectral density distribution moments of H_0 may be written as

$$M_q^{(0)} = \sum_{k_1 k_2 \ldots k_q}^{N} \frac{1}{D} \sum_L^D \langle L | h_{k_1} h_{k_2} \ldots h_{k_q} | L \rangle. \tag{37}$$

The last equation may alternatively be expressed in the form

$$M_q^{(0)} = \sum_{C(q)} \frac{q!}{m_1! m_2! \cdots m_N!} \frac{1}{D} \sum_L^D \langle L | h_1(1)^{m_1} h_2(2)^{m_2} \cdots h_N(N)^{m_N} | L \rangle \tag{38}$$

where $\{m_i\}_{i=1}^{N} = 0, 1, \ldots, q$ and the sum is extended over all compositions $C(q)$ of q, i.e. over all collections $m_1, m_2, \ldots, m_N$ such that

$$m_1 + m_2 + \cdots + m_N = q. \tag{39}$$

Let us note that zeros are included in the compositions. Using (7) and (26) we obtain

$$M_q^{(0)} = \sum_{C(q)} \frac{q!}{m_1! m_2! \cdots m_N!} \mu_{m_1 0}(1) \mu_{m_2 0}(2) \cdots \mu_{m_N 0}(N) \tag{40}$$

where the moments correspond to h rather than to h' or h'' and $\mu_{00} = 1$.

The polynomial coefficients in (40) do not depend upon the order of $\{m_i\}_{i=1}^{N}$, i.e. they are labelled by the *partitions* $\pi(q)$ of q rather than by the *compositions*. Therefore it is convenient to transform (40) so that the terms corresponding to the same partition are put together. Let

$$\pi(q) = [n_1^{v_1} n_2^{v_2} \cdots n_\lambda^{v_\lambda}] \tag{41}$$

be a partition of q consisting of

$$v = \sum_{i=1}^{\lambda} v_i \tag{42}$$

parts $n_1, n_2, \ldots, n_\lambda$ with n_i being repeated v_i times and

$$n_1 > n_2 > \cdots > n_\lambda \geq 1.$$

It is clear that

$$q = \sum_{i=1}^{\lambda} v_i n_i \tag{43}$$

and (40) may be rewritten as

$$M_q^{(0)} = \sum_{\pi(q)} \frac{q!}{(n_1!)^{v_1} (n_2!)^{v_2} \cdots (n_\lambda!)^{v_\lambda}} \mathcal{M}_\pi^{(0)} \tag{44}$$

with

$$\mathcal{M}_\pi^{(0)} = \sum_{\{v_1\}, \{v_2\}, \ldots, \{v_\lambda\}} \prod_{j=1}^{\lambda} \prod_{l_j}^{\{v_j\}} \mu_{n_j 0}(l_j). \tag{45}$$

The sum is extended over all different sets $\{v_1\}, \{v_2\}, \ldots, \{v_\lambda\}$ yield by the π partition. The symbol

$$\prod_{l_j=1}^{\{v_j\}}$$

in (45) means that l_j extends over the set $\{v_j\}$ of v_j integers, $1 \leq l_j \leq N$, and $\{v_{j_1}\} \cap \{v_{j_2}\} = \emptyset$ for all $j_1 \neq j_2$.

In the majority of applications most important are several lowest moments,

determined by terms associated with a few types of partitions. For example, if $\pi(q) = [q]$, then

$$\mathcal{M}_{[q]}^{(0)} = \sum_{r=1}^{N} \mu_{q0}(i). \tag{46}$$

If $\pi(q)$ consists of two *different* parts, i.e. if $\pi(q) = [nm]$ then

$$\mathcal{M}_{[nm]}^{(0)} = \sum_{i_1 \neq i_2}^{N} \mu_{n0}(i_1)\mu_{m0}(i_2). \tag{47}$$

If $\pi(q) = [n^m]$, then

$$\mathcal{M}_{[n^m]}^{(0)} = \sum_{i_1 > i_2 \cdots > i_m}^{N} \mu_{n0}(i_1)\mu_{n0}(i_2) \cdots \mu_{n0}(i_m). \tag{48}$$

Since $\mu_{10}(k) = 0$, $(k = 1, 2, \ldots, N)$, only these partitions in which $n_\lambda \neq 1$ contribute to (44) and (45).

In particular, for the lowest moments $(q \leq 6)$ we get

$$M_2^{(0)} = \mathcal{M}_{[2]}^{(0)} \tag{49}$$

$$M_3^{(0)} = \mathcal{M}_{[3]}^{(0)} \tag{50}$$

$$M_4^{(0)} = \mathcal{M}_{[4]}^{(0)} + 6\mathcal{M}_{[2^2]}^{(0)} \tag{51}$$

$$M_5^{(0)} = \mathcal{M}_{[5]}^{(0)} + 10\mathcal{M}_{[32]}^{(0)} \tag{52}$$

$$M_6^{(0)} = \mathcal{M}_{[6]}^{(0)} + 15\mathcal{M}_{[42]}^{(0)} + 20\mathcal{M}_{[3^2]}^{(0)} + 90\mathcal{M}_{[2^3]}^{(0)}. \tag{53}$$

3.3. The two-particle operators

Introducing a cumulative index

$$J = \frac{k(k-1)}{2} + l \qquad k \geqslant l \tag{54}$$

Hamiltonian H may be expressed as (cf. (4))

$$H = \sum_{J=1}^{R} \Lambda_J \omega_J \tag{55}$$

where $R = N(N+1)/2$. Similarly to the case of the one-particle operators, (36) may be written in the form

$$M_q = \sum_{C(q)} \frac{q!}{m_1! m_2! \cdots m_R!} \frac{\Lambda}{D} \sum_{L}^{D} \langle L | \omega_1^{m_1} \omega_2^{m_2} \cdots \omega_R^{m_R} | L \rangle \tag{56}$$

where

$$\Lambda = \prod_{J=1}^{R} \Lambda_J^{m_J} \tag{57}$$

and for the time being commutation of the operators ω has been assumed.

In order to express the N-particle moments in terms of the one-particle ones, we have to collect together those one-particle operators which depend upon the same variable. Since

$$\Lambda_{kk}\omega_{kk}(k, k) = h_k(k) \tag{58}$$

and

$$\omega_{kl}(k, l) = f_k(k)f_l(l) \qquad \text{for } k \neq l \tag{59}$$

we have to this end split the cumulative index J and reorder the one-particle operators. As can easily be checked

$$h_n(n) = \Lambda_r \omega_r \qquad \text{with } r = n(n+1)/2. \tag{60}$$

Each f_n is associated with $N-1$ different operators ω_J: ω_{n1}, $\omega_{n2}, \ldots, \omega_{nn-1}$, ω_{n+1n}, $\omega_{n+2n}, \ldots, \omega_{Nn}$. Let us denote $J(n)_i$, $i = 1, 2, \ldots, N-1$, the sequence of J corresponding to a given f_n. Then,

$$J(n)_i = \begin{cases} n(n-1)/2 + i & \text{if } 1 \leq i \leq n-1 \\ i(i+1)/2 + n & \text{if } n \leq i \leq N-1 \end{cases} \tag{61}$$

and (56) reads

$$M_q = \sum_{C(q)} \frac{\Lambda q!}{m_1! m_2! \cdots m_R!} \mu_{m_3 t_1}(h_1^{m_1} f_1^{t_1}) \mu_{m_3 t_2}(h_2^{m_2} f_2^{t_2}) \cdots \mu_{m_R t_N}(h_N^{m_R} f_N^{t_N}) \tag{62}$$

where

$$\Lambda = \Lambda_{21}^{m_2} \Lambda_{31}^{m_4} \Lambda_{32}^{m_5} \cdots \Lambda_{N,N-1}^{m_{R-1}} \tag{63}$$

and

$$t_n = \sum_{i=1}^{N-1} m[J(n)_i] \tag{64}$$

with $m[j] \equiv m_j$. For example, if $N = 5$, then $r = 1, 3, 6, 10, 15$ and

$$t_1 = m_2 + m_4 + m_7 + m_{11}$$

$$t_2 = m_2 + m_5 + m_8 + m_{12}$$

$$t_3 = m_4 + m_5 + m_9 + m_{13}$$

$$t_4 = m_7 + m_8 + m_9 + m_{14}$$

$$t_5 = m_{11} + m_{12} + m_{13} + m_{14}.$$

Equation (62), as in the case of the one-particle operators, may be simplified by changing the sum over compositions to a sum over partitions:

$$M_q \doteq \sum_{\pi(q)} \frac{q!}{(n_1!)^{v_1}(n_2!)^{v_2} \cdots (n_\lambda!)^{v_\lambda}} \mathcal{M}_\pi. \tag{65}$$

In particular

$$M_2 = \mathcal{M}_{[2]} + 2\mathcal{M}_{[1^2]} \tag{66}$$

$$M_3 = \mathcal{M}_{[3]} + 3\mathcal{M}_{[21]} + 6\mathcal{M}_{[1^3]} \tag{67}$$

with

$$\mathcal{M}_{[2]} = \mathcal{M}_{[2]}^{(0)} + \sum_{i>j}^{N} \Lambda_{ij}^2 \mu_{02}(i)\mu_{02}(j) \tag{68}$$

$$\mathcal{M}_{[1^2]} = 0 \tag{69}$$

$$\mathcal{M}_{[3]} = \mathcal{M}_{[3]}^{(0)} + \sum_{i>j}^{N} \Lambda_{ij}^3 \mu_{03}(i)\mu_{03}(j) \tag{70}$$

$$\mathcal{M}_{[21]} = \sum_{i \neq j}^{N} \Lambda_{ij}^2 \mu_{12}(i)\mu_{02}(j) \tag{71}$$

$$\mathcal{M}_{[1^3]} = \sum_{i>j}^{N} \Lambda_{ij}\mu_{11}(i)\mu_{11}(j) + \sum_{i>j>k}^{N} \Lambda_{ij}\Lambda_{jk}\Lambda_{ki}\mu_{02}(i)\mu_{02}(j)\mu_{02}(k). \tag{72}$$

Let us note that, opposite to the case of the one-particle operators, moments $\mathcal{M}_\pi$ corresponding to partitions containing 1, in general do not vanish.

The formulae in which only μ_{0n} and μ_{n0} appear, are not affected by the assumption that the operators h_k and f_k commute. In particular, if $\pi(q) = [q]$, then $C(q)$ consists of compositions for which one element in the set $\{m_i\}_{i=1}^{R}$ is equal to q while the remaining ones are equal to zero. Therefore

$$\mathcal{M}_{[q]} = \mathcal{M}_{[q]}^{(0)} + \sum_{i>j}^{N} \Lambda_{ij}^q \mu_{0q}(i)\mu_{0q}(j). \tag{73}$$

In general, if the operators do not commute, $\mu_{mn}(i)$ should be replaced by $\bar{\mu}_{mn}(i)$. In particular, in (71)

$$\bar{\mu}_{12}(i) = \frac{1}{d_i} \sum_{p=1}^{d_i} \langle i_p | \tfrac{1}{3}(h_i f_i^2 + f_i h_i f_i + f_i^2 h_i) | i_p \rangle$$

has to replace $\mu_{12}(i)$ and in Eq. (72) $\bar{\mu}_{11}(i)$, $\bar{\mu}_{11}(j)$ have to replace $\mu_{11}(i)$, $\mu_{11}(j)$. In the case of $\pi = [mn]$, $m \neq n$, equation (62) yields

$$\mathcal{M}_{[mn]} = \mathcal{M}_{[mn]}^{(0)} + \sum_{i \neq j}^{N} [\Lambda_{ij}^{n} \bar{\mu}_{mn}(i)\mu_{0n}(j) + \Lambda_{ij}^{m} \bar{\mu}_{nm}(i)\mu_{0m}(j)]$$

$$+ \sum_{k}^{N} \sum_{i>j}^{N}{}' [\Lambda_{ij}^{n} \mu_{m0}(k)\mu_{0n}(i)\mu_{0n}(j) + \Lambda_{ij}^{m} \mu_{n0}(k)\mu_{0m}(i)\mu_{0m}(j)]$$

$$+ \sum_{k}^{N} \sum_{i>j}^{N}{}' \Lambda_{ki}^{m} \Lambda_{kj}^{n} \mu_{0,\,m+n}(k)\mu_{0m}(i)\mu_{0n}(j)$$

$$+ \sum_{k>i}^{N} \sum_{i>j}^{N}{}' \Lambda_{ki}^{m} \Lambda_{ij}^{n} \mu_{0m}(k)\mu_{0m}(i)\mu_{0n}(l)\mu_{0n}(j) \tag{74}$$

where Σ' means that all the indices in the multiple sums are different. A similar formula is obtained for $\pi = [n^2]$:

$$\mathcal{M}_{[n^2]} = \mathcal{M}_{[n^2]}^{(0)} + \sum_{i \neq j}^{N} \Lambda_{ij}^{n} \bar{\mu}_{nn}(i)\mu_{0n}(j)$$

$$+ \sum_{k}^{N} \sum_{i>j}^{N}{}' \Lambda_{ij}^{n} \mu_{n0}(k)\mu_{0n}(i)\mu_{0n}(j)$$

$$+ \sum_{k}^{N} \sum_{i>j}^{N}{}' \Lambda_{ki}^{n} \Lambda_{kj}^{n} \mu_{0,\,2n}(k)\mu_{0n}(i)\mu_{0n}(j)$$

$$+ \sum_{k>i}^{N} \sum_{i>j}^{N}{}' \Lambda_{ki}^{n} \Lambda_{ij}^{n} \mu_{0n}(k)\mu_{0n}(i)\mu_{0n}(l)\mu_{0n}(j)$$

Explicit expressions for $\mathcal{M}_{\pi}$ corresponding to other partitions may be derived in an analogous way.

The one-particle moments can easily be evaluated either analytically (in the case of the harmonic or Morse oscillators) or numerically. In effect, the energy level density distributions may be approximated, without much effort, by several-moment frequency functions. Practical applications of this formalism will be presented in a forthcoming paper.

Acknowledgements

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