On a Generating Function and its Probability Distributions: 
A Contribution to the Theory of Transition Rates II

Hans Kupka

Institut für Theoretische Chemie, Heinrich-Heine-Universität Düsseldorf, D-40593 Düsseldorf, Germany

Reprint requests to Prof. H. K.; E-mail: jjkupka@gmx.de

Z. Naturforsch. 61a, 469 – 485 (2006); received January 27, 2006

A previous theory of integer-valued probability distributions is extended to many dimensions, to develop a really systematic way of treating mode mixing. The mixing of the vibrational components arises through the rotation of the normal coordinates and consequently by mixing of the parameter components in consequence of a linear relationship. The multidimensional distribution (MD), is derived with the aid of a 2N-dimensional generating function (GF), which is holomorphic in a polydisc $D^{2N}(0,1)$, and the expansion of which in a multiple power series leads to coefficients, which are values of a MD for several occupation number sets $(n_1,n_2,...,n_N)$ or $(m_1,m_2,...,m_N)$. Symmetry or invariance properties of the MD in respect to the exchange of parameters and the exchange of the occupation number sets $(n_1,n_2,...,n_N)$ and $(m_1,m_2,...,m_N)$ are investigated. For the special case, if the mixing matrix is a unit matrix, the multidimensional GF reduces to a product of one-dimensional GFs, each of which depends on parameters and complex variables of one separate component only. The advantages and disadvantages of this separation will be discussed. For illustrative purpose, relief plots of the MD are presented, demonstrating the effect of mode mixing.

Key words: Generating Function; Function of Several Complex Variables; Multidimensional Probability Distributions; Transition Probabilities.

1. Introduction

The multidimensional distribution (MD), which we described in Sections 2 and 3 of the preceding paper [1] (hereafter called I) is appropriate for a set of separable vibrational modes $\{n_k\}$, especially for components of a degenerate vibration. (The name “separable” is something of a misnomer. Normal modes are called separable if their coordinates in the electronic excited state vs. ground state are parallel shifted. Otherwise, normal modes have not only shifted origins and different frequencies in the electronic excited state, but they may also be rotated relative to the normal modes of the ground electronic state. Such modes are said to be not separable or not parallel with each other.) Here $\{n_k\}$ indicates the set of choices of $n_1,n_2,...,n_N$, where each $n_k$ can assume all integer values between zero and $n$, and for which $n_1 + n_2 + ... + n_N = n$. The individual $n_k$ can be treated as the occupation number of the $k^{th}$ separate vibrational mode. The characteristic behaviour of such multidimensional distributions is that they arise via a convolution of one-dimensional distributions, each of which is associated with an individual vibrational mode.

Quite often we are dealing with systems involving many mixed (or not separable) vibrational components, being in a state vector characterized by a set of choices of $n_1,n_2,...,n_N$, where each $n_k$ can take all integer values $\geq 0$. The formalism just outlined is applied to this case, where many $(N)$ vibrational modes of a molecule are not separable with each other in the sense that their parameters or some of them are connected by a linear relationship (i.e., by the Duschinsky rotation [2]). The multidimensional distributions of this kind differ in an essential manner from those of separable vibrational modes. Again as before, the mathematical formulation of such a concept is best carried out by using the generating function (GF) technique. By expanding the latter in a multiple-power series, this leads to coefficients which are values of an MD, for several sets $(n_1,n_2,...,n_N)$ of occupation numbers. The latter are highly complex compared to those for separable vibrational modes. This is because the number of parameters appearing in the generating function increases considerably and, as mentioned above, the parameters become dependent. Therefore, in this case, we cannot hope to obtain solutions in closed form as in the one-dimensional case, and it is necessary to develop suit-
able methods. This can be formulated in terms of recurrence equations (there is one for each occupation number \( n_k \)). This and related problems will be discussed in the next section for the case \( N = 2 \). In the last section, the result of Section 2 will be extended to the case of \( N \) vibrational components, where \( N \) is any integer.

2. The Two-Dimensional Distribution

\[ I_2 \left( \frac{m_1 m_2}{n_1 n_2} ; \frac{\Delta_1 \Delta_2}{B_1 B_2} \right) \]

Just as in Section 2 of paper I, we can examine the behaviour of the integer-valued probability distributions of two vibrational modes by considering the generating function derived in [2–4]:

\[ G_2(w_1, w_2; z_1, z_2) = 4 \beta_1^{1/2} \beta_2^{1/2} \exp \left[ \frac{A(w_1, w_2; z_1, z_2)}{B_1(w_1, w_2; z_1, z_2)} \right] \]

(1)

where \( w_1, w_2, z_1, z_2 \) are complex variables in the polydisc [5] \( |w_1| < 1, |z_1| < 1, \mu = 1, 2 \) and

\[ A(w_1, w_2; z_1, z_2) = \sum_{\mu_1 \mu_2 = 0}^1 \sum_{v_1 v_2 = 0}^1 \delta_{\mu_1 \mu_2} \beta_1 w_1^{\mu_1} w_2^{\mu_2} z_1^{v_1} z_2^{v_2}, \]

(2)

\[ B_1(w_1, w_2; z_1, z_2) = \sum_{\mu_1 \mu_2 = 0}^1 \sum_{v_1 v_2 = 0}^1 a_{\mu_1 \mu_2} \beta_2 w_1^{\mu_1} w_2^{\mu_2} z_1^{v_1} z_2^{v_2}, \]

(3)

\[ B_2(w_1, w_2; z_1, z_2) = \sum_{\mu_1 \mu_2 = 0}^1 \sum_{v_1 v_2 = 0}^1 b_{\mu_1 \mu_2} \beta_1 w_1^{\mu_1} w_2^{\mu_2} z_1^{v_1} z_2^{v_2}. \]

(4)

The quantities \( \delta_{\mu_1 \mu_2} v_1 v_2, a_{\mu_1 \mu_2} v_1 v_2 \) and \( b_{\mu_1 \mu_2} v_1 v_2 \) in the expressions (2), (3) and (4), which constitute tensors of the fourth rank, are real and given by

\[ \delta_{\mu_1 \mu_2} v_1 v_2 = (-1)^{\mu_1 + v_1 + v_2} \beta_1 \Delta_1^2 + (-1)^{\beta_1 + v_1 + v_2} \beta_2 \Delta_2^2 \]

(5)

\[ a_{\mu_1 \mu_2} v_1 v_2 = (-1)^{\mu_1 + v_1 + v_2} \beta_1 \beta_2 + (-1)^{\mu_1 + v_1} \beta_2 \Delta_2^2 + (-1)^{\beta_1 + v_1} \beta_1 \Delta_1^2 \]

(6)

\[ b_{\mu_1 \mu_2} v_1 v_2 = (-1)^{\mu_1 + v_1 + v_2} a_{\mu_1 \mu_2} v_1 v_2, \]

(7)

and

\[ \|a_v\|^2 = \left( \begin{array}{c} a_{01} \\ a_{02} \end{array} \right)^{-1} \left( \begin{array}{c} 1 \\ \omega \end{array} \right), \]

(8)

is an orthogonal matrix.

These are functions of eight dimensionless parameters, namely four positive \( \beta \) parameters, \( \beta_1, \beta_2, \beta_{12}, \beta_{21} \), and four \( \Delta \) parameters, which are real numbers. In our special case, where the matrix (8) is orthogonal, the latter are reduced to three independent parameters \( \Delta_1, \Delta_2, \phi \), where \( \phi \) is a rotation angle which parameterizes the matrix (8) (see later). In the treatment of [2, 3] and [4], (1) describes the vibrational overlap between two electronic states, the origins of which are displaced in the configuration space by \( \Delta_1, \Delta_2 \) and rotated by the angle \( \phi \). Moreover, the transition is accompanied by two vibronic components, the frequency variables or strictly the frequency changes (when going from one electronic state to another) of which are described by the \( \beta \) parameters. In this connection it was convenient to define the quantities \( \beta \) in terms of quantities of direct physical interest \( \beta_\mu = \omega_\mu / \hbar (\mu = 1, 2) \), where \( \omega_\mu \) is the angular frequency of the \( \mu \)th vibrational component in the \( s \)-electronic state as follows (including the initial and final):

\[ \beta_1 = \beta_{1(}^{(e)} / \beta_{1(}^{(i)}, \quad \beta_2 = \beta_{2(}^{(e)} / \beta_{2(}^{(i)}, \]

\[ \beta_{12} = \beta_{1(}^{(e)} / \beta_{2(}^{(i)}, \quad \beta_{21} = \beta_{2(}^{(e)} / \beta_{1(}^{(i)}. \]

(9)

Similarly, the various \( \Delta \) parameters were related to dimensioned (displacement) parameters conventionally written in terms of lengths \( k_1 \) and \( k_2 \) :

\[ \Delta_1^2 = \beta_{1}^{(e)} k_1^2, \quad \Delta_2^2 = \beta_{2(}^{(e)}, k_2^2 \]

\[ \Delta_{12} = \beta_{12}^{(e)} k_1^2, \quad \Delta_{21} = \beta_{21}^{(e)} k_2^2. \]

(10)

where

\[ \left( \begin{array}{c} k_1' \\ k_2' \end{array} \right) = \left( \begin{array}{cc} \omega_{01} & \omega_{12} \\ \omega_{21} & \omega_{02} \end{array} \right)^{-1} \left( \begin{array}{c} k_1 \\ k_2 \end{array} \right), \]

(11)

are additionally displacement parameters, generated by the matrix (8) and assigned to \( \Delta_1' \) and \( \Delta_2' \) in (10). Equations (9) to (11) denote what we mean by the term not separable (or not parallel) vibrational modes. This dependence is manifested, as will be clearly seen later, by the appearance of cross factors \( \beta_{12} \) and \( \beta_{21} \), as well as by the appearance of \( k_1' \) and \( k_2' \).
2.1. Properties of $\delta_{\mu_1,\mu_2;v_1,v_2}$, $\mu_{\mu_1,\mu_2;v_1,v_2}$ and $b_{\mu_1,\mu_2;v_1,v_2}$

First, note that the 16 components of the tensor $\delta_{\mu_1,\mu_2;v_1,v_2}$ are not independent, and we can reduce them to eight by noting that

$$\delta_{\mu_1,\mu_2;v_1,v_2} = -\delta_{1-\mu_1,1-\mu_2;1-v_1,1-v_2}. \quad (12)$$

A further reduction is accomplished with the help of the relations

$$\begin{align*}
\delta_{00,00} + \delta_{00,10} + \delta_{00,01} + \delta_{00,11} &= 0, \\
\delta_{01,00} + \delta_{01,10} + \delta_{01,01} + \delta_{01,11} &= 0, \\
\delta_{10,00} + \delta_{10,10} + \delta_{10,01} + \delta_{10,11} &= 0, \\
\delta_{11,00} + \delta_{11,10} + \delta_{11,01} + \delta_{11,11} &= 0,
\end{align*} \quad (13)$$

in which the last two relations result from the first two by taking relation (12) into account. This indicates that 6 independent components are required to specify the generating function. It can be reduced still further to $5$, if we assume that the matrix (8) is orthogonal.

Similarly, it follows directly from (6) that $a_{\mu_1,\mu_2;v_1,v_2}$ is not altered by the interchanges $\mu_1 \to 1-\mu_1$, $\mu_2 \to 1-\mu_2$, $v_1 \to 1-v_1$, $v_2 \to 1-v_2$. Thus it is sufficient to specify the values of $a_{\mu_1,\mu_2;v_1,v_2}$ for the two values of the pair $(\mu_1,\mu_2)$ and the same two values of the pair $(v_1,v_2)$. Further relations, similar to (13), reduce their number to $2$:

$$\begin{align*}
a_{00,00} + a_{00,10} + a_{00,01} + a_{00,11} &= 4\beta_1\beta_2, \\
a_{01,00} + a_{01,10} + a_{01,01} + a_{01,11} &= -4\beta_1\beta_2, \\
a_{10,00} + a_{10,10} + a_{10,01} + a_{10,11} &= -4\beta_1\beta_2, \\
a_{11,00} + a_{11,10} + a_{11,01} + a_{11,11} &= 4\beta_1\beta_2.
\end{align*} \quad (14)$$

Finally, according to (7), we obtain in the same manner

$$\begin{align*}
b_{00,00} + b_{00,10} + b_{00,01} + b_{00,11} &= 4, \\
b_{01,00} + b_{01,10} + b_{01,01} + b_{01,11} &= -4, \\
b_{10,00} + b_{10,10} + b_{10,01} + b_{10,11} &= -4, \\
b_{11,00} + b_{11,10} + b_{11,01} + b_{11,11} &= 4.
\end{align*} \quad (15)$$

2.2. Case $w_1 = w_2 = 0$

Before we analyze in more detail the generating function $G_2$ and the corresponding distributions, let us consider the special case $w_1 = w_2 = 0$. In that case we obtain from (1)

$$G_2 \left( 0,0,z_1,z_2 \right) = \left( 1,1,\beta_1,\beta_2,\beta_{12},\beta_{21} \right) \exp \left[ \frac{-\delta_{00,00} + \delta_{00,10} + \delta_{00,01} + \delta_{00,11} + \delta_{01,01} + \delta_{01,11} + \delta_{10,01} + \delta_{10,11}}{2} \right]. \quad (16)$$

which represents the kernel of $G_2(w_1,w_2,z_1,z_2)$. The mathematical subtleties in two dimensions, though, are more difficult than they are in one. The functions $G_1(0,z)$ and $G_2(0,0,z_1,z_2)$ exhibit a remarkable regularity. This is manifested in the similarity of the functions with respect to their exponents, which have the same structural feature. (They have the topology of a torus of the dimension one for $N = 1$ and of two for $N = 2$, respectively.) Both of them vanish when $z = 1$ or $z_1 = z_2 = 1$, respectively. Analogously to the one-dimensional case, the mapping of the bidisc

$$G_2 \left( w_1,w_2,z_1,z_2 \right) \Delta_1,\Delta_2,\beta_1,\beta_2,\beta_{12},\beta_{21} \right) = \sum_{m_1,m_2}^{\infty} \sum_{n_1,n_2}^{\infty} I_2 \left( m_1,m_2; n_1,n_2; \Delta_1,\Delta_2,\beta_1,\beta_2,\beta_{12},\beta_{21} \right) w_1^{m_1} w_2^{m_2} z_1^{n_1} z_2^{n_2}, \quad (17)$$

where $I_2 \left( m_1,m_2; n_1,n_2 \right)$ is, as will be shown below, for each pair of nonnegative integers $(m_1,m_2)$ a 2-dimensional probability distribution of $n_1,n_2$. In (17), the dependence of the generating functions and their distributions on the parameters are shown explicitly. For the physical situation described above, we can set $z_\mu = \left( \begin{array}{c} 1 \end{array} \right)$.
exp(iωμt) and wμ = exp(−α/T − iωμt) (μ = 1, 2), with α being a positive number, or in another modification, zμ = exp(−α/T − iωμt), wμ = exp(iωμt), where t is a time variable.

$$G_2(w_1, w_2, z_1, z_2) = 4β_1^{1/2}B_2^{1/2}(w_1, w_2, z_1, z_2) = \exp \left[ \frac{A(w_1, w_2, z_1, z_2)}{B_1(w_1, w_2, z_1, z_2)B_2(w_1, w_2, z_1, z_2)} \right]^{1/2}. \quad (18)$$

In other words, the complex conjugate of $G_2$ is obtained simply by replacing the variables $w_μ$ and $z_μ$ by their conjugates $\bar{w}_μ$ and $\bar{z}_μ$ (μ = 1, 2). In conjunction with (17), it follows that the coefficients of the series (17), $I_2 \left( \begin{array}{c} m_1 \\ n_1 \\ m_2 \\ n_2 \end{array} \right)$, are real. In particular, $I_2 \left( \begin{array}{c} m_1 \\ n_1 \\ m_2 \\ n_2 \end{array} \right) ≥ 0$ for all pairs of levels $(m_1, m_2)$ or $(n_1, n_2)$ by definition. This point emerges clearly from the fourfold integration approach to evaluation of the generating function $G_2$ (cf. (37) of [3]). Finally it is a simple matter to verify that for each pair of levels $(m_1, m_2)$

$$\sum_{n_1, n_2=0}^∞ I_2 \left( \begin{array}{c} m_1 \\ n_1 \\ m_2 \\ n_2 \end{array} \right) = 1. \quad (19)$$

For the proof of (19) it is convenient to express $A(w_1, w_2, z_1, z_2)$ in terms of a bilinear form:

$$A(w_1, w_2, z_1, z_2) = \|w_1, w_2, w_1w_2\| \begin{pmatrix} \delta_{00,00} & \delta_{00,10} & \delta_{00,11} & \delta_{00,12} & 1 \\ \delta_{01,00} & \delta_{01,10} & \delta_{01,11} & \delta_{01,12} & z_1 \\ \delta_{10,00} & \delta_{10,10} & \delta_{10,11} & \delta_{10,12} & z_2 \end{pmatrix} \begin{pmatrix} \delta_{11,00} \\ \delta_{11,10} \\ \delta_{11,11} \\ \delta_{11,12} \end{pmatrix} = w^T [\delta_{\mu, \nu}] \|z\|,$$

where $w$ and $z$ are column matrices col(1, $w_1$, $w_2$, $w_1w_2$) and col($z_1$, $z_2$, $z_1z_2$), respectively, and $\mu = (μ_1, μ_2), ν = (ν_1, ν_2)$. The superscript T in (20) denotes transposition. This matrix approach is very convenient for the generalization to three, four, etc., dimensions. If the number of the vibrational modes becomes very large, i.e., $N$, then the order of the square matrix in (20) is $2^N$. It follows from (13) that the sum of the elements of each row, each column and any main diagonals is the same, namely zero (compare with a magic square).

Similarly, representing $B_1(w_1, w_2, z_1, z_2)$ in the form of a product of three matrices, a row, a square and a column matrix,

$$B_1(w_1, w_2, z_1, z_2) = w^T [\alpha_{\mu, \nu}] \|z\|, \quad (21)$$

where according to (14) the sum of elements in the first, second, third and fourth row of the square matrix in (21) are $4β_1β_2$, $−4β_1β_2$, $−4β_1β_2$, and $4β_1β_2$, respectively. Correspondingly the sum of elements in the first, second, third and fourth column are 4, $−4$, $−4$ and 4, respectively. Finally we note that

$$B_2(w_1, w_2, z_1, z_2) = w^T [\beta_{\mu, \nu}] \|z\|. \quad (22)$$

Here the sum of the elements in each row of $[\beta_{\mu, \nu}]$ is the same as the sum of the elements in the columns of $[\alpha_{\mu, \nu}]^T$, and vice versa.

By direct substitution in (20), (21) and (22) $z_1 = z_2 = 1$, and taking into account the above properties of $[\alpha_{\mu, \nu}]^T$, $[\alpha_{\mu, \nu}]^d$ and $[\beta_{\mu, \nu}]^T$, we have after matrix multiplication

$$A(w_1, w_2, 1, 1) = 0, \quad B_1(w_1, w_2, 1, 1) = 4β_1β_2(1 − w_1)(1 − w_2), \quad (23)$$

$$B_2(w_1, w_2, 1, 1) = 4(1 − w_1)(1 − w_2). \quad (24)$$

Note that the right-hand side of (17) converges as $z_1 \to 1$ and $z_2 \to 1$. Substituting these expressions in (1) gives:

$$G_2(w_1, w_2, 1, 1) = \frac{1}{(1 − w_1)(1 − w_2)} = \sum_{m_1, m_2=0}^∞ w_1^{m_1}w_2^{m_2}. \quad (24)$$

Comparing this result with (17), we have

$$G_2(w_1, w_2, 1, 1) = \sum_{m_1, m_2=0}^∞ \sum_{n_1, n_2=0}^∞ \sum_{m_1, m_2=0}^∞ \sum_{n_1, n_2=0}^∞ \sum_{m_1, m_2=0}^∞ \sum_{n_1, n_2=0}^∞ I_2 \left( \begin{array}{c} m_1 \\ n_1 \\ m_2 \\ n_2 \end{array} \right) w_1^{m_1}w_2^{m_2} \quad (24a)$$

which completes the proof of (19). Equation (19) underlines the correctness and generality of our definition of $I_2 \left( \begin{array}{c} m_1 \\ n_1 \\ m_2 \\ n_2 \end{array} \right)$.
Similarly, if we consider the function (1) in the polydisc $D_1(0,1)$ \( |z_\mu| < 1, |w_\mu| \leq 1, \mu = 1,2 \), we have for each pair of levels \((n_1,n_2)\)
\[
\sum_{m_1,m_2=0}^{\infty} I_2 \left( \frac{m_1 m_2}{n_1 n_2} \right) = 1. \tag{25}
\]

**Proof:** Analogously to the foregoing treatment, we have
\[
A(1,1,z_1,z_2) = 0,
B_1(1,1,z_1,z_2) = 4(1-z_1)(1-z_2),
B_2(1,1,z_1,z_2) = 4\beta_1\beta_2(1-z_1)(1-z_2), \tag{26}
\]
and this gives for the generating function (1) the series
\[
G_2(1,1,z_1,z_2) = \frac{1}{(1-z_1)(1-z_2)} = \sum_{n_1,n_2=0}^{\infty} z_1^{n_1} z_2^{n_2}. \tag{27}
\]
Expressing (17) in a different manner, we obtain
\[
G_2(1,1,z_1,z_2) = \sum_{n_1,n_2=0}^{\infty} I_2 \left( \frac{m_1 m_2}{n_1 n_2} \right) z_1^{m_1} z_2^{m_2}. \tag{27a}
\]
By comparison with the series (27) follows (25).

2.4. Symmetry properties of $I_2 \left( \frac{m_1 m_2}{n_1 n_2} \right)$

The matrix representation of $A(w_1,w_2,z_1,z_2)$ (and similarly of $B_1$ and $B_2$) introduced above allows us to investigate the question of how the distribution $I_2$ is affected by exchange of parameters. To be explicit, we will investigate the behaviour of $I_2$ under the exchange of parameters:
\[
\Delta_1 \leftrightarrow \Delta'_1, \quad \Delta_2 \leftrightarrow \Delta'_2,
\beta_1 \leftrightarrow \beta_1^{-1}, \quad \beta_2 \leftrightarrow \beta_2^{-1}, \quad \beta_{12} \leftrightarrow \beta_{21}^{-1}. \tag{28}
\]
Using formula (5), one can prove that under the exchange (28) the coefficient matrix of the form $A(w_1,w_2,z_1,z_2)$ in (20) transforms to
\[
\|\delta_{\mu,v}\|_4^4 \rightarrow \beta_1^{-1} \beta_2^{-1} \|\delta_{\mu,v}\|_4^4, \tag{29}
\]
where the matrix on the right-hand side of (29) is the transposition of the original in (20).

Analogously, it follows from (5) and (7) that, by replacing $\beta_1$ by $\beta_1^{-1}$, $\beta_2$ by $\beta_2^{-1}$, $\beta_{12}$ by $\beta_{21}^{-1}$ and $\beta_{21}$ by $\beta_{12}^{-1}$,
\[
\|a_{\mu,v}\|_4^4 \rightarrow \beta_1^{-1} \beta_2^{-1} \|a_{\mu,v}\|_4^4, \tag{30}
\]
and similarly
\[
\|b_{\mu,v}\|_4^4 \rightarrow \beta_1^{-1} \beta_2^{-1} \|b_{\mu,v}\|_4^4. \tag{31}
\]
where use has been made of the fact that the matrix elements of (8) obey $\alpha_{11}^2 = \alpha_{22}^2 = \cos^2 \phi$ and $\alpha_{12}^2 = \sin^2 \phi$.

If we now simultaneously interchange the variables $(w_1,w_2) \leftrightarrow (z_1,z_2)$, the following relations hold:
\[
A(w_1,w_2,z_1,z_2) = w^T \|\delta_{\mu,v}\|_4^4 z,
\beta_1^{-1} \beta_2^{-1} z^T \|\delta_{\mu,v}\|_4^4 w = \beta_1^{-1} \beta_2^{-1} w^T \|\delta_{\mu,v}\|_4^4 z, \tag{32}
\]
\[
B_1(w_1,w_2,z_1,z_2) = w^T \|a_{\mu,v}\|_4^4 z
\beta_1^{-1} \beta_2^{-1} z^T \|a_{\mu,v}\|_4^4 w = \beta_1^{-1} \beta_2^{-1} w^T \|a_{\mu,v}\|_4^4 z, \tag{33}
\]
\[
B_2(w_1,w_2,z_1,z_2) = w^T \|b_{\mu,v}\|_4^4 z
\beta_1^{-1} \beta_2^{-1} z^T \|b_{\mu,v}\|_4^4 w = \beta_1^{-1} \beta_2^{-1} w^T \|b_{\mu,v}\|_4^4 z. \tag{34}
\]
Combining (32) to (34), we have
\[
\frac{A(w_1,w_2,z_1,z_2)}{B_1(w_1,w_2,z_1,z_2)} = \frac{A(z_1,z_2,w_1,w_2)}{B_1(z_1,z_2,w_1,w_2)},
\]
and correspondingly
\[
G_2 \left( \frac{w_1 w_2 z_1 z_2}{z_1 z_2 w_1 w_2} \right) \begin{vmatrix} \Delta_1, \Delta_2 \ \\ \beta_1, \beta_2 \end{vmatrix} = \begin{vmatrix} \Delta'_1, \Delta'_2 \ \\ \beta_1^{-1}, \beta_2^{-1} \end{vmatrix} \begin{vmatrix} \beta_{12}, \beta_{21} \end{vmatrix}. \tag{35}
\]
If we now expand both sides of the identity (35) in the polydisc $D^4(0, r)$ according to (17) in a power series and equate the terms of $w_1^{m_1} w_2^{m_2} z_1^{n_1} z_2^{n_2}$, we have the

**Corollary 1.** The distribution $I_2$ is left invariant by the exchange of the parameters in (28), provided the integer variables $m_\mu$ and $n_\mu$ are simultaneously exchanged:
\[
I_2 \left( \frac{m_1 m_2}{n_1 n_2} \right) \begin{vmatrix} \Delta_1, \Delta_2 \ \\ \beta_1, \beta_2 \end{vmatrix} = \begin{vmatrix} \Delta'_1, \Delta'_2 \ \\ \beta_1^{-1}, \beta_2^{-1} \end{vmatrix} \begin{vmatrix} \beta_{12}, \beta_{21} \end{vmatrix}. \tag{36}
\]
Equation (36) is a generalization of (30) in paper I and indicates that there exists no mirror images in respect to \((m_1, m_2) \leftrightarrow (n_1, n_2)\) (i.e., between emission and absorption) owing to the presence of the cross parameters \(\beta_{12}\) and \(\beta_{21}\) in (36), as well as the fact that \(\Delta^\prime_{\mu} \neq \Delta_{\mu}\). This holds only, if the rotation angle \(\phi = 0\) and the frequency changes \(\Delta \beta = 0\) (see below).

Similarly, since the indices 1 and 2 in (17) are indistinguishable, they can exchange roles:

\[
I_2 \left( \frac{m_1 m_2}{n_1 n_2}; \Delta_1, \Delta_2; \beta_{12}, \beta_{21} \right) = \frac{1}{\beta_{12}},
\]

and

\[
B_2(w_1, w_2, z_1, z_2) = \prod_{\mu=1}^2 \left[ \beta_{1}(1+w_{\mu})(1-z_{\mu}) + (1+w_{\mu})(1-z_{\mu}) \right].
\]

Dividing \(A\) by \(B_1\), we find that

\[
\frac{A(w_1, w_2, z_1, z_2)}{B_1(w_1, w_2, z_1, z_2)} = \frac{\beta_1 \Delta^2_1 (1-w_1)(1-z_1)}{\beta_1 (1-w_1)(1+z_1) + (1+w_1)(1+z_1)} + \frac{\beta_2 \Delta^2_2 (1-w_2)(1-z_2)}{\beta_2 (1-w_2)(1+z_2) + (1+w_2)(1+z_2)},
\]

where the right-hand side breaks down into two terms, each of which depends on variables \(w_{\mu}, z_{\mu}\) and parameters \(\Delta_{\mu}\) and \(\beta_{\mu}\) of only one component \(\mu\) (the cross parameters \(\beta_{12}\) and \(\beta_{21}\) disappear). Thus in the case \(\phi = 0\), the 2-dimensional GF can simply be written as a product of two single mode GFs:

\[
G_2(w_1, w_2, z_1, z_2) = G_1(w_1, z_1)G_1(w_2, z_2),
\]

where

\[
G_1(w, z) = 2\beta^{1/2} \frac{\exp \left[ -\frac{\beta \Delta^2 (1-w)(1-z)}{\beta(1-w)(1+z) + (1+w)(1-z)} \right]}{[(1+\beta^2)(1-w^2)(1-z^2) + 2\beta(1+w^2)(1+z^2) - 4wz)]^{1/2}}
\]

is clearly the one-dimensional GF considered in paper I. (For a direct comparison with the one-dimensional GF (1) defined in paper I, we have to set \(\frac{1-\beta}{1+\beta} = b\) and \(\frac{1-\beta^2}{1+\beta^2} = a\).

The result obtained can be stated as follows:

**Corollary 2.** If \(\phi = 0\), the two-dimensional GF \(G_2(w_1, w_2, z_1, z_2)\) factors into a product of one-dimensional terms \(G_1\), each of which depends on variables and parameters belonging to one component only. If in addition \(\beta_1 = \beta_2\), then the 2-dimensional distribution \(I_2\) generated by (38) coincides with formula (35) of paper I.

2.5. Case \(\phi = 0\)

If \(\phi = 0\), it follows from (8) to (11) that \(k_{\mu} = k_\mu\) and \(\Delta_{\mu}^2 = \beta_{\mu} \Delta_{\mu}^2\) (\(\mu = 1, 2\)). In this special case (2) to (7) can be written as follows:

\[
A(w_1, w_2, z_1, z_2) = \beta_1 \Delta^2_1 (1-w_1)(1-z_1) + \beta_2 \Delta^2_2 (1-w_2)(1-z_2),
\]

where

\[
B_1(w_1, w_2, z_1, z_2) = \prod_{\mu=1}^2 \left[ \beta_{1}(1-w_{\mu})(1+z_{\mu}) + (1+w_{\mu})(1-z_{\mu}) \right].
\]

2.6. Numerical Results

As already mentioned in the introduction, the most convenient way to perform the calculation of \(I_2\) is by means of recurrence equations (there is one for each of the occupation numbers \(m_1\) and \(n_1\)). Such a system of recurrence equations, as well as the calculation procedure have been treated in detail [4].
and we will now use them to calculate the effect of the rotation angle $\phi$ on $I_2$. Note that if $\phi \neq 0$, the two vibrational components are mutually interdependent, which is manifested in an unusual behaviour of the distribution $I_2$. This is illustrated in Figs. 1–4, which represents relief plots of $I_2 \left( \frac{m_1 m_2}{n_1 n_2} \right)$ over the plane $(n_1, n_2)$ for various pairs $(m_1, m_2)$ and moderately large parameters $\Delta_1 = \Delta_2 = 4$. In the patterns shown in Figs. 1 and 2 there are two maxima, i.e., if $m_1 = 1$ and $m_2 = 0$ or $m_1 = 0$ and $m_2 = 1$, respectively. If the parameters $\Delta_1$ and $\Delta_2$ are sufficiently large, then the number of maxima increases as $m_1 + m_2$ increases (see Figs. 3 and 4). Generally, $m_1$ and $m_2$ coincides with the number of valleys, which for $\phi = 0$ run perpendicular to the $n_1$ or $n_2$ axes, respectively. Furthermore, if the angle $\phi$ changes, a renormalization among the modes occurs and the maximum (maxima) of $I_2$ moves in the $(n_1, n_2)$ plane, running, for special values of $\phi$, close to the $n_1$ axis or close to the $n_2$ axis. In these special cases (i.e., $\phi = 30^\circ$ and $\phi = 120^\circ$), the distribution $I_2$ becomes more complex and behaves as a one-dimensional distribution with a remarkably complicated course. Finally, note that $I_2$ is periodic in $\phi$ with the period $\pi$.

When $\Delta_1$ and $\Delta_2$ are small ($\Delta \mu \leq 1$), it is difficult to plot the surface of $I_2$ graphically, since $I_2$ falls nearly exponentially as the numbers $n_1$ and $n_2$ rise. In this case, the maximum of $I_2$ lies in the vicinity of $n_1 = m_1$, $n_2 = m_2$. As the angle $\phi$ varies, this maximum moves, as before, towards the $n_1$ axis, then from the $n_1$ axis to the $n_2$ axis, returning at $\phi = 180^\circ$ to the initial position for $\phi = 0^\circ$. 

Fig. 1. Relief plots of $I_2 \left( \frac{m_1 m_2}{n_1 n_2} \Delta_1, \Delta_2, \beta_1, \beta_2 \right)$ for $m_1 = 1$, $m_2 = 0$. The chosen parameters are: $\Delta_1 = \Delta_2 = 4$ and $\beta_1 = 0.9$, $\beta_2 = 1.18$, $\beta_{12} = 0.53$ and $\beta_{21} = 2.0$. The values of the angle $\phi$ are indicated in the figure.
3. General Case of $N$ Degrees of Freedom

We now proceed to the general case $I_N$ ($N$ = any integer). Just as in the preceding section, we use the generating function previously derived [3, 4]. The only difference from the treatment in Section 2 is, that now the generating function has a higher dimension, which depends on $2^N$ complex variables $w_{\mu}, z_{\mu}$ ($\mu = 1, 2, \ldots, N$). The infinite series representation of the latter in a polydisc $D^{2N}(0, 1) \mid |w_{\mu}| < 1, |z_{\mu}| < 1, \mu = 1, 2, \ldots, N$ generates an infinite sequence of distributions, which depend on $2N$ integer variables $m_i \geq 0, n_i \geq 0, (i = 1, 2, \ldots, N)$. We will show that the distributions so obtained obey conditions similar to those of (19) and (25), but generalized to $2N$ integer variables. Simultaneously, we show how the symmetry properties of the distribution, analogously to equation (36) for $N = 2$, can be extended to the general case of $2N$ arguments. Taking into account the dependence on the parameters, the generating function is

$$G_N(w_1, w_2, \ldots, w_N, z_1, z_2, \ldots, z_N) =$$

$$2^N \prod_{\mu=1}^{N} (\beta_{\mu}^{(e)} \beta_{\mu}^{(l)})^{1/2} \exp \frac{-A(w_1, w_2, \ldots, w_N, z_1, z_2, \ldots, z_N)}{B_1(w_1, w_2, \ldots, w_N, z_1, z_2, \ldots, z_N)B_2(w_1, w_2, \ldots, w_N, z_1, z_2, \ldots, z_N)^{1/2}}$$ (39)
where

\[
A(w_1, w_2, \ldots, w_N, z_1, z_2, \ldots, z_N) = \sum_{\mu_1, \mu_2, \ldots, \mu_N} \sum_{v_1, v_2, \ldots, v_N} \delta_{\mu_1, \mu_2, \ldots, \mu_N, v_1, v_2, \ldots, v_N} w_1^{\mu_1} w_2^{\mu_2} \cdots w_N^{\mu_N} z_1^{v_1} z_2^{v_2} \cdots z_N^{v_N},
\]

(40)

\[
B_1(w_1, w_2, \ldots, w_N, z_1, z_2, \ldots, z_N) = \sum_{\mu_1, \mu_2, \ldots, \mu_N} \sum_{v_1, v_2, \ldots, v_N} a_{\mu_1, \mu_2, \ldots, \mu_N, v_1, v_2, \ldots, v_N} w_1^{\mu_1} w_2^{\mu_2} \cdots w_N^{\mu_N} z_1^{v_1} z_2^{v_2} \cdots z_N^{v_N},
\]

(41)

and

\[
B_2(w_1, w_2, \ldots, w_N, z_1, z_2, \ldots, z_N) = \sum_{\mu_1, \mu_2, \ldots, \mu_N} \sum_{v_1, v_2, \ldots, v_N} b_{\mu_1, \mu_2, \ldots, \mu_N, v_1, v_2, \ldots, v_N} w_1^{\mu_1} w_2^{\mu_2} \cdots w_N^{\mu_N} z_1^{v_1} z_2^{v_2} \cdots z_N^{v_N}.
\]

(42)

The coefficients \( \delta_{\mu_1, \mu_2, \ldots, \mu_N, v_1, v_2, \ldots, v_N}, a_{\mu_1, \mu_2, \ldots, \mu_N, v_1, v_2, \ldots, v_N} \) and \( b_{\mu_1, \mu_2, \ldots, \mu_N, v_1, v_2, \ldots, v_N} \), which can be regarded as elements of matrices of order \( 2^N \), are real and given by

Fig. 3. Same as Fig. 1 but for \( m_1 = 2, m_2 = 0 \).
\[
\delta \mu_1 \mu_2 \ldots \mu_N, v_1 v_2 \ldots v_N = \sum_{1 \leq j_p \leq N} (-1)^{\mu_1 + \mu_2 + \ldots + \mu_N + v_{j_p} + v_{j_p}} \beta_{j_p}^{(e)} \beta_{j_p}^{(l)} \beta_{j_p}^{(1)} k_{j_p j_p}^{12 \ldots N^2} \\
+ \sum_{1 \leq i_1 < i_2 \ldots < i_r} \sum_{1 \leq j_p < j_q \leq N} (-1)^{\mu_1 \mu_2 \ldots \mu_{r-1} + v_{j_p} + v_{j_q}} \beta_{i_1}^{(e)} \beta_{i_2}^{(e)} \ldots \beta_{i_{r-1}}^{(e)} \beta_{j_p}^{(1)} \beta_{j_q}^{(1)} k_{j_p j_q}^{(i_1 i_2 \ldots i_{r-1})^2} \\
+ \ldots + \sum_{1 \leq i_1 \leq N} (-1)^{\mu_1 + v_1 + \ldots + v_{i_1}} \beta_{i_1}^{(e)} \beta_{i_1}^{(l)} \beta_{i_1}^{(1)} \ldots \beta_{N}^{(l)} k_{12 \ldots N^1}^{2},
\]

where \( i_1 < i_2 < \ldots < i_r \) form a complete system of \( r \) indices as do \( j_1 < j_2 < \ldots < j_s \), both taken from the indices 1, 2, \ldots, \( N \) and where \( r + s = N + 1 \). For convenience of notation we use here the dimensioned quantities \( k_{j_1 j_2 \ldots j_q}^{i_1 i_2 \ldots i_p} \) and \( \beta_{i}^{(e)} \) and \( \beta_{i}^{(l)} \) instead of dimensionless \( \Delta_{j_1 j_2 \ldots j_q}^{i_1 i_2 \ldots i_p} \) and \( \beta_{i} \) and \( \beta_{i j} \) of the preceding section. [For \( N > 2 \), we can define alternatively dimensionless displacement parameters as follows:

\[
\Delta_{j_1 j_2 \ldots j_q}^{i_1 i_2 \ldots i_p} = k_{j_1 j_2 \ldots j_q}^{i_1 i_2 \ldots i_p} \left( \frac{\beta_{i_1}^{(e)} \beta_{i_2}^{(e)} \ldots \beta_{i_p}^{(e)}}{\beta_{1}^{(e)} \ldots \beta_{j_1-1}^{(l)} \beta_{j_1+1}^{(l)} \ldots \beta_{j_q-1}^{(l)} \beta_{j_q+1}^{(l)} \ldots \beta_{N}^{(l)}} \right)^{1/2}, \quad (1 \leq i_1 < i_2 < \ldots < i_p \leq N),
\]
where $p + q = N + 1$ and similarly frequency factors

$$
\beta_{j_1 j_2 \ldots j_p}^{(i_1 i_2 \ldots i_p)} = \frac{\beta_{j_1}^{(e)} \beta_{j_2}^{(e)} \ldots \beta_{j_p}^{(e)}}{\beta_{j_1}^{(1)} \beta_{j_2}^{(1)} \ldots \beta_{j_p}^{(1)}}.
$$

The interactive parameters $k_{j_1 j_2 \ldots j_p}^{(i_1 i_2 \ldots i_p)}$ appearing in (43) for the interactive parameters of the scheme (44) for the interactive parameters of the scheme (44) are given by

$$
k_1^{(12\ldots N)} = W \binom{23\ldots N}{23\ldots N} k_{12\ldots N}^{(1)} - W \binom{13\ldots N}{23\ldots N} k_{12\ldots N}^{(2)} + \ldots + (-1)^{N+1} W \binom{12\ldots N-1}{23\ldots N} k_{12\ldots N}^{(N)},
$$

$$
k_2^{(12\ldots N)} = -W \binom{23\ldots N}{13\ldots N} k_{12\ldots N}^{(1)} + W \binom{13\ldots N}{13\ldots N} k_{12\ldots N}^{(2)} + \ldots + (-1)^{N+2} W \binom{12\ldots N-1}{13\ldots N} k_{12\ldots N}^{(N)},
$$

$$
\vdots
$$

$$
k_N^{(12\ldots N)} = (-1)^{N+1} W \binom{23\ldots N}{12\ldots N-1} k_{12\ldots N}^{(1)} + \ldots + (-1)^{2N} W \binom{12\ldots N-2}{12\ldots N-1} k_{12\ldots N}^{(N)},
$$

$$
k_{12}^{(i_1 i_2 \ldots i_{N-1})} = W \binom{i_2 i_3 \ldots i_{N-1}}{34\ldots N} k_{12\ldots N}^{(i_1)} - W \binom{i_1 i_3 \ldots i_{N-1}}{34\ldots N} k_{12\ldots N}^{(i_2)} + \ldots + (-1)^N W \binom{i_1 i_2 \ldots i_{N-2}}{34\ldots N} k_{12\ldots N}^{(i_{N-1})},
$$

$$
k_{13}^{(i_1 i_2 \ldots i_{N-1})} = -W \binom{i_2 i_3 \ldots i_{N-1}}{24\ldots N} k_{12\ldots N}^{(i_1)} + W \binom{i_1 i_3 \ldots i_{N-1}}{24\ldots N} k_{12\ldots N}^{(i_2)} + \ldots + (-1)^N+1 W \binom{i_1 i_2 \ldots i_{N-2}}{24\ldots N} k_{12\ldots N}^{(i_{N-1})},
$$

$$
\vdots
$$

$$
k_{N-1,N}^{(i_1 i_2 \ldots i_{N-1})} = (-1)^{1/2(N-1)} W \binom{i_2 i_3 \ldots i_{N-1}}{12\ldots N-2} k_{12\ldots N}^{(i_1)} + \ldots + (-1)^{1/2(N+1)} W \binom{i_1 i_2 \ldots i_{N-2}}{12\ldots N-2} k_{12\ldots N}^{(i_{N-1})},
$$

for all combinations of $N-1$ indices $1 \leq i_1 < i_2 < \ldots < i_{N-1} \leq N$ selected from the indices $1, 2, \ldots, N$ and arranged in lexicographic order.

$$
\vdots
$$

and finally

$$
k_{12\ldots N-1}^{(i_1 i_2)} = W \binom{i_2}{N} k_{12\ldots N-1}^{(i_1)} - W \binom{i_1}{N} k_{12\ldots N-1}^{(i_2)},
$$

$$
k_{12\ldots N-2,N}^{(i_1 i_2)} = -W \binom{i_2}{N-1} k_{12\ldots N-1}^{(i_1)} + W \binom{i_1}{N-1} k_{12\ldots N-1}^{(i_2)},
$$

$$
\vdots
$$

$$
k_{23\ldots N}^{(i_1 i_2)} = (-1)^{N+1} W \binom{i_2}{1} k_{12\ldots N}^{(i_1)} + (-1)^N W \binom{i_1}{1} k_{12\ldots N}^{(i_2)} \quad (1 \leq i_1 < i_2 \leq N).
$$

Here $W_{j_1 j_2 \ldots j_p}^{(i_1 i_2 \ldots i_p)}$ are minors of order $p$ of the $N$-dimensional orthogonal matrix $\|a_j\|^N$. The upper indices refer to the rows and the subindices to the columns of the matrix $\|a_j\|^N$. As can be seen, the construction of the scheme (44) for the interactive parameters $k_{j_1 j_2 \ldots j_p}^{(i_1 i_2 \ldots i_p)}$ due to mixing of components is simple. These parameters are derivable from the components of the displacement vector $k_{12\ldots N}$ in combination with minors of $\|a_j\|^N$ of decreasing order. Moreover, as the order of the minors is decreased, the number
of the components of $k_{12...N}$ on the right-hand side of equations (44) is successively diminished by 1. In the language of matrix theory [6], the coefficients in the system of (44a) are, apart from the sign $\pm$, elements of the $(N-1)$th compound matrix of $||a_{ij}||_1^N$. Those of the system (44b) are elements of the $(N-2)$th compound matrix, and so on, until the first compounds matrix [cf. (44x)] is achieved. Next, we observe that the upper and lower indices of $k_{12...N}$ (44) have a close relationship with the indices of the minors $W (i_{12...N})$. Thus the additional parameters on the left-hand side of (44) are elements of the matrix $||a_{ij}||_1^N$ and the vector $k_{12...N}$. The total number of these parameters is $\sum_{k=1}^{N}(N-k)$, which evidently increases rapidly with the number of components $N$. From the relation (44) it can also be inferred that a reversion of the vector $k_{12...N}$ leaves the GF (39) invariant, since all components $k_{12...N}$ as well as those generated by the effect of $||a_{ij}||_1^N$ enter the expression (40) as squares. Since $W (i_{12...N})$ are minors of an orthogonal matrix, (44a) can be written more compactly as

$$k_{12...N} = ||a_{ij}||_1^{-1} k_{12...N}.$$  \hspace{1cm} (45)

Equation (45) is a generalization of (11) to $N$ dimensions.

Similarly we have

$$a_{\mu_1\mu_2...\mu_N\nu_1\nu_2...\nu_N} = (-1)^{\mu_1+\mu_2+...+\mu_N} W(12...N) \sum_{1\leq i_1<i_2<...<i_{N-1}\leq N} \sum_{1\leq j_p\leq N} \sum_{1\leq i_q\leq N} (-1)^{i_1+i_2+...+i_{N-1}+j_p} W(i_1,i_2,...,i_{N-1},j_p,j_{p+1},...,j_N) \sum_{\beta_1^{(e)}...\beta_N^{(e)}} \beta_1^{(e)} \beta_2^{(e)}...\beta_N^{(e)} \beta_1^{(l)} \beta_2^{(l)}...\beta_N^{(l)}.$$  \hspace{1cm} (46)

$$+ \sum_{1\leq i_1<i_2<...<i_{N-2}\leq N} \sum_{1\leq j_p\leq N} \sum_{1\leq i_q\leq N} (-1)^{i_1+i_2+...+i_{N-2}+j_p} W(i_1,i_2,...,i_{N-2},j_p,j_{p+1},...,j_N) \sum_{\beta_1^{(e)}...\beta_{N-2}^{(e)}\beta_{N-1}^{(l)}\beta_N^{(l)}} \beta_1^{(e)} \beta_2^{(e)}...\beta_{N-2}^{(e)}\beta_{N-1}^{(l)} \beta_N^{(l)} + \sum_{1\leq i_1<i_2<...<i_{N-1}\leq N} (-1)^{i_1+i_2+...+i_{N-1}} \beta_1^{(l)} \beta_2^{(l)}...\beta_N^{(l)},$$

and finally

$$b_{\mu_1\mu_2...\mu_N\nu_1\nu_2...\nu_N} = (-1)^{\mu_1+\mu_2+...+\mu_N+\nu_1+\nu_2+...+\nu_N} a_{\mu_1\mu_2...\mu_N\nu_1\nu_2...\nu_N}.$$  \hspace{1cm} (47)

### 3.1 Properties of $\delta_{\mu,\nu}$, $a_{\mu,\nu}$ and $b_{\mu,\nu}$

Representing the expression (40) in a bilinear form, analogously to equation (20) of the preceding section, we have

$$A(w_1,w_2,...,w_N,z_1,...,z_N) = w^T \|\delta_{\mu,\nu}\|_1^N z,$$  \hspace{1cm} (48)

where the first subscript $\mu = (\mu_1,\mu_2,...,\mu_N)$ denotes the row, and the second subscript $\nu = (\nu_1,\nu_2,...,\nu_N)$ the column containing the element $\delta_{\mu,\nu}$. $w$ and $z$ are column matrices with the elements arranged in some definite, e. g., lexicographic order

$$w = \begin{pmatrix} 1 \\ w_1 \\ \vdots \\ w_N \\ w_1 w_2 \\ \vdots \\ w_{N-1} w_N \\ w_1 w_2 w_3 \\ \vdots \\ w_1 w_2 w_3 \ldots w_N \end{pmatrix}, \quad z = \begin{pmatrix} 1 \\ z_1 \\ \vdots \\ z_N \\ z_1 z_2 \\ \vdots \\ z_{N-1} z_N \end{pmatrix}.$$  

In this representation, the matrix $\|\delta_{\mu,\nu}\|_1^N$ behaves like a magic square, since the sum of elements in each row and column and any main diagonal is the same, namely zero:
\[ \sum_{v_1, v_2, \ldots, v_N = 0}^1 \delta_{\mu_1 \mu_2 \ldots \mu_N} v_1 v_2 \cdots v_N = 0, \]  
(49a)

for each row with the subscript \( \mu = (\mu_1, \mu_2, \ldots, \mu_N) \)

and

\[ \sum_{\mu_1, \mu_2, \ldots, \mu_N = 0}^1 \delta_{\mu_1 \mu_2 \ldots \mu_N} v_1 v_2 \cdots v_N = 0, \]  
(49b)

for each column with the subscript \( \nu = (v_1, v_2, \ldots, v_N). \)

The properties (49) follow directly from (43) and are analogous to the relation (13) of the preceding section.

Now, with the same treatment regarding the form

\[ B_1(w_1, w_2, \ldots, w_N) = w_T \| a_{\mu, \nu} \|_{1}^{2N} z, \]  
(50)

we establish some properties of the matrix \( \| a_{\mu, \nu} \|_{1}^{2N}. \)

Starting from the fundamental formula (46), we have for the sum of the elements of the row with the subscript \( \mu = (\mu_1, \mu_2, \ldots, \mu_N) \)

\[ \sum_{v_1, v_2, \ldots, v_N = 0}^1 a_{\mu_1 \mu_2 \ldots \mu_N} v_1 v_2 \cdots v_N = (-1)^{\mu_1 + \cdots + \mu_N} 2^N \beta_1^{(e)} \beta_2^{(e)} \cdots \beta_N^{(e)}, \]  
(51a)

and analogously

\[ \sum_{\mu_1, \mu_2, \ldots, \mu_N = 0}^1 a_{\mu_1 \mu_2 \ldots \mu_N} v_1 v_2 \cdots v_N = (-1)^{\nu_1 + \cdots + \nu_N} 2^N \beta_1^{(e)} \beta_2^{(e)} \cdots \beta_N^{(e)}, \]  
(51b)

for the sum of the elements of the column with the subscript \( \nu = (v_1, v_2, \ldots, v_N). \)

To complete our development, we finally write

\[ B_2(w_1, w_2, \ldots, w_N) = w_T \| b_{\mu, \nu} \|_{1}^{2N} z, \]  
(52)

On the basis of formulae (46) and (47), we find that now

\[ \sum_{v_1, v_2, \ldots, v_N = 0}^1 b_{\mu_1 \mu_2 \ldots \mu_N} v_1 v_2 \cdots v_N = (-1)^{\mu_1 + \mu_2 + \cdots + \mu_N} 2^N \beta_1^{(e)} \beta_2^{(e)} \cdots \beta_N^{(e)}, \]  
(53a)

where \( \mu = (\mu_1, \mu_2, \ldots, \mu_N) \) denotes the subscript of the row being considered, and

\[ \sum_{\mu_1, \mu_2, \ldots, \mu_N = 0}^1 b_{\mu_1 \mu_2 \ldots \mu_N} v_1 v_2 \cdots v_N = (-1)^{\nu_1 + \nu_2 + \cdots + \nu_N} 2^N \beta_1^{(e)} \beta_2^{(e)} \cdots \beta_N^{(e)}, \]  
(53b)

where \( \nu = (v_1, v_2, \ldots, v_N) \) denotes the subscript of the selected column.

### 3.2. The Sum Rules

Before proceeding, we note that the generating function (39) is holomorphic in the polydisc \( D^{2N}(0, 1) \) and can be developed in a power series as follows:

\[ G_N(a_1, a_2, \ldots, a_N, z_1, z_2, \ldots, z_N) = \sum_{m_1, m_2, \ldots, m_N = 0}^\infty \sum_{n_1, n_2, \ldots, n_N = 0}^\infty \frac{I_N(m_1 m_2 \cdots m_N)}{w_1^{m_1} w_2^{m_2} \cdots w_N^{m_N} z_1^{n_1} z_2^{n_2} \cdots z_N^{n_N}}, \]  
(54)

where \( I_N \) is, as will be shown, for each choice of integers \( (m_1, m_2, \ldots, m_N) \) an \( N \)-dimensional probability distribution of \( n_1, n_2, \ldots, n_N \), and vice versa. Throughout the rest of this section \( m_1, m_2, \ldots, m_N \) and \( n_1, n_2, \ldots, n_N \) signify any integers \( \geq 1 \). With the help of the expressions (48), (50) and (52), we can now establish the following theorems.

**Theorem 1.** For each choice of integers \( (m_1, m_2, \ldots, m_N) \)

\[ \sum_{n_1, n_2, \ldots, n_N = 0}^\infty I_N(m_1 m_2 \cdots m_N) = 1. \]  
(55)

**Proof.** The proof of this remarkable theorem offers no difficulty, following closely the lines of the proof of the corresponding identity for \( N = 2 \). By direct substitution in (46), (50) and (52) \( z_1 = z_2 = \ldots = z_N = 1 \), we have, according to (49a), (51a) and (53a),

\[ A(w_1, w_2, \ldots, w_N, 1, 1, \ldots, 1) = 0, \]

\[ B_1(w_1, w_2, \ldots, w_N, 1, 1, \ldots, 1) = 2^N \beta_1^{(e)} \beta_2^{(e)} \cdots \beta_N^{(e)}, \]

and

\[ \sum_{\mu_1, \mu_2, \ldots, \mu_N = 0}^1 (-1)^{\mu_1 + \mu_2 + \cdots + \mu_N} w_1^{\mu_1} w_2^{\mu_2} \cdots w_N^{\mu_N} = 2^N \beta_1^{(e)} \beta_2^{(e)} \cdots \beta_N^{(e)} (1 - w_1)(1 - w_2) \cdots (1 - w_N), \]  
(56)
and

\[ B_2(w_1, w_2, \ldots, w_N, 1, 1, \ldots, 1) = 2^N \beta_1^{(1)} \beta_2^{(1)} \cdots \beta_N^{(1)} \]

\[ \cdot \sum_{\mu_1, \mu_2, \ldots, \mu_N=0}^{1} (-1)^{\mu_1+\mu_2+\ldots+\mu_N} w_1^{\mu_1} w_2^{\mu_2} \cdots w_N^{\mu_N} \]

\[ = 2^N \beta_1^{(1)} \beta_2^{(1)} \cdots \beta_N^{(1)} (1-w_1)(1-w_2) \cdots (1-w_N). \]

Substituting these expressions in (39), we obtain

\[ G_N(w_1, w_2, \ldots, w_N, 1, 1, \ldots, 1) = \prod_{\nu=1}^{N} \frac{1}{1-z_\nu} = \sum_{m_1, m_2, \ldots, m_N=0}^{\infty} \left( \prod_{n_1, n_2, \ldots, n_N=0}^{\infty} I_N \left( \frac{m_1 m_2 \cdots m_N}{n_1 n_2 \cdots n_N} \right) \right) w_1^{m_1} w_2^{m_2} \cdots w_N^{m_N}. \]

(57)

On the other hand, from (54), we have

\[ B_1(1, 1, \ldots, 1, z_1, z_2, \ldots, z_N) \]

\[ = 2^N \beta_1^{(1)} \beta_2^{(1)} \cdots \beta_N^{(1)} \]

\[ \cdot \sum_{\nu_1, \nu_2, \ldots, \nu_N=0}^{\infty} (-1)^{\nu_1+\nu_2+\ldots+\nu_N} z_1^{\nu_1} z_2^{\nu_2} \cdots z_N^{\nu_N} \]

\[ = 2^N \beta_1^{(1)} \beta_2^{(1)} \cdots \beta_N^{(1)} (1-z_1)(1-z_2) \cdots (1-z_N), \]

(60)

\[ B_2(1, 1, \ldots, 1, z_1, z_2, \ldots, z_N) \]

\[ = 2^N \beta_1^{(e)} \beta_2^{(e)} \cdots \beta_N^{(e)} \]

\[ \cdot \sum_{\nu_1, \nu_2, \ldots, \nu_N=0}^{\infty} (-1)^{\nu_1+\nu_2+\ldots+\nu_N} z_1^{\nu_1} z_2^{\nu_2} \cdots z_N^{\nu_N} \]

\[ = 2^N \beta_1^{(e)} \beta_2^{(e)} \cdots \beta_N^{(e)} (1-z_1)(1-z_2) \cdots (1-z_N). \]

(61)

which proves the theorem. Equation (55) is a generalization of (19) of the preceding section.

Regarding the function (1) in the polydisc \( D^{2N}(0, 1) \)
\[ \text{with} \quad |w_\mu| \leq 1, \quad |z_\mu| < 1; \quad \mu = 1, 2, \ldots, N, \]

the same procedure as before enables us to prove the following supplementary:

**Theorem 2.**

\[ \sum_{m_1, m_2, \ldots, m_N=0}^{\infty} I_N \left( \frac{m_1 m_2 \cdots m_N}{n_1 n_2 \cdots n_N} \right) = 1, \]

(59)

which is valid for each choice of integers \((n_1, n_2, \ldots, n_N)\).

**Proof.** Based on (48), (50) and (52) and the relations (49b), (51b) and (53b), we have after direct substitution of \(w_1 = w_2 = \ldots = w_N = 1\)

Substituting these expressions in (39), we obtain

\[ G_N(1, 1, \ldots, 1, z_1, z_2, \ldots, z_N) = \prod_{\nu=1}^{N} \frac{1}{1-z_\nu} = \sum_{n_1, n_2, \ldots, n_N=0}^{\infty} \left( \prod_{n_1, n_2, \ldots, n_N=0}^{\infty} I_N \left( \frac{m_1 m_2 \cdots m_N}{n_1 n_2 \cdots n_N} \right) \right) \]

\[ = \sum_{n_1, n_2, \ldots, n_N=0}^{\infty} \frac{z_1^{n_1} z_2^{n_2} \cdots z_N^{n_N}}{1-z_1^{n_1} z_2^{n_2} \cdots z_N^{n_N}}. \]

(62)

On the other hand, (54) gives

\[ G_N(1, 1, \ldots, 1, z_1, z_2, \ldots, z_N) = \sum_{n_1, n_2, \ldots, n_N=0}^{\infty} \left( \prod_{n_1, n_2, \ldots, n_N=0}^{\infty} I_N \left( \frac{m_1 m_2 \cdots m_N}{n_1 n_2 \cdots n_N} \right) \right) \]

\[ = \sum_{n_1, n_2, \ldots, n_N=0}^{\infty} \frac{z_1^{n_1} z_2^{n_2} \cdots z_N^{n_N}}{1-z_1^{n_1} z_2^{n_2} \cdots z_N^{n_N}}. \]

(61)

what completes the proof of (59).

### 3.3. Symmetry Property of \( I_N \)

In a manner similar to the preceding section, we investigate below the invariance of \( I_N \) under the transition of parameters:

\[ \beta_1^{(1)} \leftrightarrow \beta_1^{(e)}, \quad \mu = 1, 2, \ldots, N \]

(63)

change of parameters:

\[ k_{12, \ldots, N} \leftrightarrow k_{12, \ldots, N} \]

First, we note that the replacement of \( k_{12, \ldots, N} \) by \( k_{12, \ldots, N} \)
requires, according to relation (45), that \( \| \omega_j \| \rightarrow \| \omega_j \|^{-1} \). Thus, starting with the vector \( k_{12..N}^{(i_1i_2..ip)} \) and the inverse matrix \( \| \omega_j \|^{-1} \) instead of \( k_{12..N} \) and \( \| \omega_j \| \), we have the following lemma.

**Lemma 1.** If we replace in (44) the vector \( k_{12..N}^{(i_1i_2..ip)} \) by \( k_{12..N}^{(i_1i_2..ip)} \) and the orthogonal matrix by its inverse, then the interactive displacement parameters convert into

\[
k_{12..N}^{(i_1i_2..ip)} \rightarrow \pm k_{12..N}^{(j_1j_2..j_p)}, \quad \left( 1 \leq i_1 < i_2 < \ldots < i_p \right) \leq N \quad (64)
\]

In other words, the transformation (64) consists of exchanging the lower and upper indices of \( k_{j_1j_2..j_q}^{(i_1i_2..ip)} \) with each other.

Indeed, starting for instance with the first equation of (44b), we have

\[
k_{12..N}^{(i_1i_2..i_p)} = W^{-1} \left( \begin{array}{c} k_{12..N}^{(i_1i_2..i_p)} \\ \vdots \\ k_{12..N}^{(p)} \end{array} \right) = W^{-1} \left( \begin{array}{c} k_{12..N}^{(i_1i_2..i_p)} \\ \vdots \\ k_{12..N}^{(p)} \end{array} \right) = \cdots = (-1)^{N-1} W^{-1} \left( \begin{array}{c} k_{12..N}^{(i_1i_2..i_p)} \\ \vdots \\ k_{12..N}^{(p)} \end{array} \right)
\]

and

\[
\left( 1 \leq i_1 < i_2 < \ldots < i_p \right) \leq N
\]
where we have made use of the facts that the minor of the inverse matrix of \( \|a_{ij}\|_1^N \) for arbitrary 
\[ 1 \leq i_1 < i_2 < \ldots < i_p \leq N \] is

\[ W^{-1} \begin{pmatrix} i_1 & i_2 & \cdots & i_p \\ j_1 & j_2 & \cdots & j_p \end{pmatrix} = (-1)^{\sum_{i=1}^{p} j_i + \sum_{j=1}^{p} i_j} W \begin{pmatrix} j_1' & j_2' & \cdots & j_{N-p}' \\ i_1' & i_2' & \cdots & i_{N-p}' \end{pmatrix}, \]

where \( i_1 < i_2 < \ldots < i_p \) and \( i'_1 < i'_2 < \ldots < i'_{N-p} \) form a complete system of indices 1, 2, \ldots, \( N \), as \( j_1 < j_2 < \ldots < j_p \) and \( j'_1 < j'_2 < \ldots < j'_{N-p} \) [6], and that any of the summands containing \( k_{i_1j_2 \ldots j_q}^{(i'_1j'_2 \ldots j'_{N-p})} \), where \( i \geq 3 \), is zero.

In the same manner we find for the remaining coefficient matrices appearing in the GF

\[ \|a_{\mu,\nu}\|_1^{2N} \rightarrow \|a_{\mu,\nu}\|_1^{2N} \] (65b)

and

\[ \|b_{\mu,\nu}\|_1^{2N} \rightarrow \|b_{\mu,\nu}\|_1^{2N} \] (65c)

Finally, if we exchange, as in the preceding section, simultaneously the role of the variables \( z_\mu \leftrightarrow w_\mu \) (\( \mu = 1, 2, \ldots, N \)), then we obtain

\[ I_N \left( m_1 \ldots m_N \mid n_1 \ldots n_N \right) \{ k_{i_1j_2 \ldots j_q}^{(i'_1j'_2 \ldots j'_{N-p})} \} ; \{ \beta_\mu^{(e)}, \beta_\mu^{(l)} \} \right) = G_N(z_1, \ldots, z_N, w_1, \ldots, w_N) \left( m_1 \ldots m_N \mid n_1 \ldots n_N \right) \{ k_{i_1j_2 \ldots j_q}^{(i'_1j'_2 \ldots j'_{N-p})} \} ; \{ \beta_\mu^{(l)}, \beta_\mu^{(e)} \}, \] (66)

of the special case

\[ \|a_{ij}\|_1^N = \|\delta_{ij}\|_1^N, \] (68)

where \( \delta_{ij} \) is the Kronecker delta. In this case all minors in the system of equations (44) and (46) vanish, except those of the principal minors, which are 1. Hence the system of equations (44) simplifies considerably, since

\[ k_{i_1 \ldots j_q}^{(i'_1j'_2 \ldots j'_{N-p})} = k_{i_1 \ldots j_q} \] (69)

and

\[ k_{i_1j_2 \ldots j_q}^{(i'_1j'_2 \ldots j'_{N-p})} = \pm k_{i_1j_2 \ldots j_q} \]

if \( j_1, j_2, \ldots, j_q \) completed by \( i_1, i_2, \ldots, i_p \) form a complete sequence 1, 2, \ldots, \( N \) and where \( i'_r = (\text{rest of } i'_s) \), or

\[ k_{i_1j_2 \ldots j_q}^{(i'_1j'_2 \ldots j'_{N-p})} = 0 \]

otherwise.
From this it follows that
\[
\frac{A(w_1,w_2,\ldots,w_N,z_1,\ldots,z_N)}{B_1(w_1,w_2,\ldots,w_N,z_1,\ldots,z_N)} = \frac{\prod_{\mu=1}^{N} \beta_{\mu}^{(e)}(1-w_{\mu})(1+z_{\mu}) + \beta_{\mu}^{(i)}(1+w_{\mu})(1-z_{\mu})}{\prod_{\mu=1}^{N} \beta_{\mu}^{(i)}(1-w_{\mu})(1+z_{\mu}) + \beta_{\mu}^{(i)}(1+w_{\mu})(1-z_{\mu})},
\]

and

\[
G_N(w_1,w_2,\ldots,w_N,z_1,\ldots,z_N) = \prod_{\mu=1}^{N} G_{1}(w_{\mu},z_{\mu}), \quad (70)
\]

where \(G_{1}(w,z)\) is again the one-dimensional GF considered in I. Thus we have the following:

**Theorem 4.** If the matrix (68) is a unit matrix, then the multidimensional GF \(G_N\) factors into a simple product of \(N\) one-dimensional GFs, each of which depends on variables and parameters of one vibrational component only. If in addition the parameters \(\beta_{\mu}^{(e)}/\beta_{\mu}^{(i)} = \beta_{\mu}\) for all components \(\mu\) are equal, the corresponding distribution \(I_N\) generated by (70) coincides with formula (35) of paper I.

4. Concluding Remarks

The explicit separation of vibrations in the multidimensional GF of Theorem 4 allows an effective reduction of the number of degrees of freedom and facilitates the calculation of transition rates. In this regard, it cannot be too strongly emphasized that the calculation of transition rates in the parallel mode approximation has a fundamental inadequacy that is evident from the derivation above. The defect emerges, if we return to the case of \(N\) vibrational modes amongst which some are not parallel with each other. This situation occurs if the latter have the same symmetry, especially if they are totally symmetric in the molecular group. In this case, the complexity introduced by the interactive displacements [(44b)-(44x)] is considerable and this fact cannot be overlooked in any “parallel mode estimate” of the transition probability. Even with considerable effort, it is impossible to factor the exact GF into a product of one-dimensional GFs. Note that the interactive displacements parameters are not quantities with physical significance. They merely represent the error incurred in making a crude approximation, assuming that all modes are parallel. Another remarkable feature of mode mixing is the dependence of the transition rate on the cross-frequency parameters, see (46). (Note that in the parallel mode approximation the transition rate depends solely upon \(k_{\mu}\) and \(\beta_{\mu} = \omega_{\mu}^{(e)}/\omega_{\mu}^{(i)}\) per mode.) Both of these findings are manifested in the molecular spectra: (i) A striking energy narrowing or broadening of the absorption and fluorescence spectra does occur [2], (ii) regularly structured emission bands (in form of single mode progressions) occur only at special values of \(\phi\), especially when the (orthogonal) matrix \(|\omega_{\mu}|_{1}^{N}\) is a unit matrix. Under all other conditions, lines in the spectra are more or less scrambled and irregularly distributed.