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Invariant expansion. IV. The exponentials of tensorial expressions

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The expansion of the exponential of a tensorial expression such as the interaction or pair correlation function between two nonspherical molecules 1, 2 is of the form $\Sigma_{mnl}\,\lambda^{mnl}\Phi^{mnl}(12)$, where $\Phi^{mnl}(12)$ are invariant tensorial expressions that depend only on the orientation of 1 and 2. The generating function $e^{-\Sigma_{mnl}\lambda^{mnl}\Phi^{mnl}} = \Sigma_{pqt}\, i^{pqt}(\lambda)\Phi^{pqt}$ defines a generalized Bessel function (GBF). We discuss integral representations and recurrence relations for the GBF. The first GBFs for dipolar and linear quadrupolar exponents, which are of interest in the theory of ionic solutions are computed explicitly.

I. INTRODUCTION

In the theory of molecular liquids, the linear approximation (in most cases the mean spherical approximation, MSA), is often not accurate, and one needs to include in the treatment nonlinear functions of the interaction potential. These functions are, in almost all cases exponential. For example, in the Percus–Yevick (PY) or hypernetted chain (HNC) equations,[1] we encounter expressions of the form

$$e^{-W}, \tag{1.1}$$

where $W = W(12)$ is a trace, or invariant contraction of a tensor form.

For the PY:

$$W = \beta U, \tag{1.2}$$

where β is the Boltzmann thermal factor and $U = U(12)$ is the potential energy between molecules 1 and 2. It is a function of the position $\mathbf{r}_{12}$ and the orientation given by the Euler angles $\mathbf{\Omega} = \alpha, \beta, \gamma$.

For the HNC we need

$$W = \beta U - h + c, \tag{1.3}$$

where $h = h(12)$ and $c = c(12)$ are the indirect and direct correlation functions.[1] Expressions of the exponential form are found in other theories of fluids of nonspherical molecules.[2–4]

The recent work of Patey[5] and co-workers on the numerical solution of the HNC equation for fluids with nonspherical molecules, has shown that this equation yields excellent results for the thermodynamics and structure of dipolar hard spheres and hard ellipsoids. One of the difficulties in solving the HNC is the evaluation of an exponential like Eq. (1.1). In his work, Patey used differentiation to transform the HNC closure relation into an integral that contains W, h, c, and a coupling coefficient which contains a $9J$ symbol. More recently, Caillol[6] has shown, that one could avoid the integration step using angular momentum operators.

In the present work, we undertake a systematic study of the generalized Bessel functions (GBF), which are generated by the function

$$g = e^{-W} = e^{-\Sigma\lambda^{pqt}\Phi^{pqt}} = \sum_{mnl} i^{mnl}(\lambda)\Phi^{mnl}(12). \tag{1.4}$$

The strategy proposed to compute the GBFs is to compute the first member i^{000} by integration, and to generate the higher members by recursion relations. In the most general case a fivefold integration is necessary to calculate i^{000}. However, a significant reduction in the number of integrations can be achieved by a factorization technique described below. For the linear dipole case we need only one single integral of a modified spherical Bessel function. For linear quadrupoles we require a double integration of a cylindrical Bessel function.

II. BASIC FORMALISM

Consider a function $W(12)$ of the position and orientation of 1 and 2. We write

$$W(12) = \sum \lambda_{\mu\nu}^{mnl}\Phi_{\mu\nu}^{mnl}(12), \tag{2.1}$$

where λ is, in general, a function of the intermolecular distance r_{12} and the rotational invariants are[7]

$$\Phi^{mnl} = \Phi_{\mu\nu}^{mnl}(12) = [(2m+1)(2n+1)]^{1/2} \times \sum_{\mu'\nu'\lambda'} \begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} R^{m}_{\mu\mu'}(\mathbf{\Omega}_1) R^{n}_{\nu\nu'}(\mathbf{\Omega}_2) R^{l}_{\lambda'0}(\hat{r}_{12}), \tag{2.2}$$

where we have used (following Patey[5]) the functions $R^{m}_{\mu\mu'}(\mathbf{\Omega})$ of Messiah[8] rather than the functions $D^{m}_{\mu\mu'}(\mathbf{\Omega})$ of Edmonds,[9] because they appear to be more reliable. They are related by

$$[D^{m}_{\mu\mu'}(\mathbf{\Omega})]^* = R^{m}_{\mu\mu'}(\mathbf{\Omega}). \tag{2.3}$$

The rotational invariants satisfy the orthogonality relation

$$(2l+1)/64\pi^4 \int d\mathbf{\Omega}_1\, d\mathbf{\Omega}_2 \Phi_{\mu'\nu'}^{m'n'l'}(12)[\Phi_{\mu\nu}^{mnl}(12)]^* = \delta_{\mu\mu'}\delta_{\nu\nu'}\delta_{ll'}\delta_{mm'}\delta_{nn'}. \tag{2.4}$$

Consider now the expansion

$$e^{-\Sigma\lambda^{m'n'l'}\Phi^{m'n'l'}} = \sum_{mnl} i^{mnl}(\lambda)\Phi^{mnl}(12), \tag{2.5}$$

where we omitted the Greek subindices for clarity, and $\boldsymbol{\lambda} = \{\lambda_{\mu\nu}^{mnl}\}$. Then

$$i^{mnl}(\lambda) = (2l+1)/64\pi^4 \int d\,\Omega_1\, d\,\Omega_2\, e^{-\Sigma\lambda^{m'n'l'}\Phi^{m'n'l'}} \times [\Phi^{mnl}(12)]^*. \quad (2.6)$$

A simpler expression is obtained when the irreducible representation[7] is used. This corresponds to using a reference frame in which the z axis is aligned with the vector $\mathbf{r}_{12}$. In this case $\theta_{12} = \phi_{12} = 0$ and

$$R^{\,l}_{\lambda 0}(0) = \delta_{\lambda 0}.$$

We get

$$W(\alpha) = \alpha^{mn}_{\chi}\Phi^{mn}_{\chi}(12), \quad (2.7)$$

where

$$\alpha^{mn}_{\chi} = \sum \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \lambda^{mnl} \quad (2.8)$$

and

$$\Phi^{mn}_{\chi} = \Phi^{mn}_{\mu\nu\chi}(12) = [(2m+1)(2n+1)]^{1/2} R^{\,m}_{\mu\chi}(\Omega)[R^{\,n}_{\nu\chi}(\Omega)]^*. \quad (2.9)$$

The orthogonality relation now reads

$$1/64\pi^4 \int d\,\Omega_1\, d\,\Omega_2\, \Phi^{m'n'}_{\mu'\nu',\chi'}(12)[\Phi^{mn}_{\mu\nu,\chi}(12)]^* = \delta_{\mu\mu'}\delta_{\nu\nu'}\delta_{\chi\chi'}\delta_{mm'}\delta_{nn'}. \quad (2.10)$$

In this representation the generating function for the GBFs is

$$e^{-\Sigma\alpha^{m'n'}_{\chi'}\Phi^{m'n'}_{\chi'}} = \sum_{mn\chi} i^{mn}_{\chi}(\alpha)\Phi^{mn}_{\chi}(12), \quad (2.11)$$

therefore, using the orthogonality relation (2.10):

$$i^{mn}_{\chi}(\alpha) = 1/64\pi^4 \int d\,\Omega_1\, d\,\Omega_2\, e^{-\Sigma\alpha^{m'n'}_{\chi'}\Phi^{m'n'}_{\chi'}} \times [\Phi^{mn}_{\chi}(12)]^*. \quad (2.12)$$

The relation between the GBF in the "1" representation and the irreducible "χ" representation is

$$i^{mn}_{\chi}(\alpha) = \sum_{l} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} i^{mnl}(\lambda). \quad (2.13)$$

III. RECURSION RELATIONS

The GBFs have recursion relations similar to those of the Bessel functions. From Eq. (2.6),

$$\frac{\partial}{\partial\lambda^{m_2n_2l_2}_{\mu_2\nu_2}} i^{m_1n_1l_1}_{\mu_1\nu_1}(\lambda) = -(2l+1)/64\pi^4 \int d\,\Omega_1\, d\,\Omega_2\, [\Phi^{m_1n_1l_1}_{\mu_1\nu_1}]^*[\Phi^{m_2n_2l_2}_{\mu_2\nu_2}]\, e^{-W}. \quad (3.1)$$

But

$$[\Phi^{m_1n_1l_1}_{\mu_1\nu_1}]^*[\Phi^{m_2n_2l_2}_{\mu_2\nu_2}] = (-)^{\mu_1+\nu_1+1}[(2m_1+1)(2n_1+1)(2m_2+1)(2n_2+1)]^{1/2} \times \sum_{mnl}(2l+1)[(2m+1)(2n+1)]^{1/2} \begin{pmatrix} m_1 & n_1 & l_1 \\ m_2 & n_2 & l_2 \\ m & n & l \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} m_1 & m_2 & m \\ \mu_1 & \mu_2 & \mu \end{pmatrix} \begin{pmatrix} n_1 & n_2 & n \\ -\nu_1 & \nu_2 & \nu \end{pmatrix} [\Phi^{mnl}_{\mu\nu}]^* \quad (3.2)$$

or

$$\frac{\partial}{\partial\lambda^{m_2n_2l_2}_{\mu_2\nu_2}} i^{m_1n_1l_1}_{\mu_1\nu_1}(\lambda) = (-)^{\mu_1+\nu_1+1}[2l_1+1][(2m_1+1)(2n_1+1)(2m_2+1)(2n_2+1)]^{1/2} \times \sum_{mnl}[(2m+1)(2n+1)]^{1/2} \begin{pmatrix} m_1 & n_1 & l_1 \\ m_2 & n_2 & l_2 \\ m & n & l^2 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} m_1 & m_2 & m \\ -\mu_1 & \mu_2 & \mu \end{pmatrix} \begin{pmatrix} n_1 & n_2 & n \\ -\nu_1 & \nu_2 & \nu \end{pmatrix} i^{mnl}_{\mu\nu}(\lambda). \quad (3.3)$$

When $m = n = l = 0$ this expression collapses to

$$\frac{\partial}{\partial\lambda^{mnl}_{\mu\nu}} i^{000}_{00}(\lambda) = (-)^{\mu+\nu+1}[2l+1] i^{mnl}_{\mu\nu}(\lambda). \quad (3.4)$$

In terms of the irreducible representations we have a somewhat simpler form. From Eq. (2.12),

$$\frac{\partial}{\partial\alpha^{m_2n_2}_{\mu_2\nu_2\chi_2}} i^{m_1n_1}_{\mu_1\nu_1\chi_1}(\alpha) = -1/64\pi^4 \int d\,\Omega_1\, d\,\Omega_2\, [\Phi^{m_1n_1}_{\mu_1\nu_1\chi_1}]^*[\Phi^{m_2n_2}_{\mu_2\nu_2\chi_2}]e^{-W}, \quad (3.5)$$

but

$$[\Phi^{m_1n_1}_{\mu_1\nu_1\chi_1}]^*[\Phi^{m_2n_2}_{\mu_2\nu_2\chi_2}] = (-)^{\mu_1+\nu_1+1}[(2m_1+1)(2n_1+1)(2m_2+1)(2n_2+1)]^{1/2}\sum_{mn}[(2m+1)(2n+1)]^{1/2} \begin{pmatrix} m_1 & m_2 & m \\ \chi_1 & \chi_2 & \chi \end{pmatrix} \begin{pmatrix} m_1 & m_2 & m \\ -\mu_1 & \mu_2 & \mu \end{pmatrix} \times \begin{pmatrix} n_1 & n_2 & n \\ -\nu_1 & \nu_2 & \nu \end{pmatrix} \begin{pmatrix} n_1 & n_2 & n \\ -\chi_1 & -\chi_2 & -\chi \end{pmatrix} [\Phi^{mn}_{\mu\nu\chi}]^*, \quad (3.6)$$

so

$$\frac{\partial}{\partial\lambda^{m_2n_2}_{\mu_2\nu_2\chi_2}} i^{m_1n_1}_{\mu_1\nu_1\chi_1}(\boldsymbol{\alpha})$$
$$= (-)^{\mu_1+\nu_1+1}[(2m_1+1)(2n_1+1)(2m_2+1)(2n_2+1)]^{1/2}\sum_{mn}[(2m+1)(2n+1)]^{1/2}\begin{pmatrix} m_1 & m_2 & m\\ \chi_1 & \chi_2 & \chi\end{pmatrix}\begin{pmatrix} m_1 & m_2 & m\\ -\mu_1 & \mu_2 & \mu\end{pmatrix}$$
$$\times\begin{pmatrix} n_1 & n_2 & n\\ -\nu_1 & \nu_2 & \nu\end{pmatrix}\begin{pmatrix} n_1 & n_2 & n\\ -\chi_1 & -\chi_2 & -\chi\end{pmatrix} i^{mn}_{\mu\nu\chi}(\boldsymbol{\alpha}) \tag{3.7}$$

which is a considerably simpler relation than Eq. (3.3) because there are less sums and no $9J$ symbol. The first member of the family yields

$$\frac{\partial}{\partial\alpha^{mn}_{\mu\nu,\chi}} i^{00}_{00,0}(\boldsymbol{\alpha}) = (-)^{\mu+\nu+1} i^{mn}_{-\mu-\nu-\chi}(\boldsymbol{\alpha}). \tag{3.8}$$

These recurrence relations are similar to those of Fries and Patey.[5]

A second type of recurrence relations, which involve no derivatives, can be obtained using raising and lowering operators[10] for the angular momentum states. This procedure is similar to that of Caillo[6]:

$$\mathbf{J}^1_{\pm} = e^{\mp\gamma_1}\left[\cot\beta_1\frac{\partial}{\partial\gamma_1} \pm \frac{\partial}{\partial\beta_1} - \frac{1}{\sin\beta_1}\frac{\partial}{\partial\alpha_1}\right],$$
$$J^1_0 = -i\frac{\partial}{\partial\gamma_1}. \tag{3.9}$$

Consider first the invariant form (2.5), operating with J^1_β where $\beta = 0$, $+$ or $-$, we get, after use of the orthogonality relation (2.4):

$$\beta_\mu i^{mnl}_{\mu\nu}(\boldsymbol{\alpha})$$
$$= (-)^{\mu+\nu+1}[2l+1][(2m+1)(2n+1)]^{1/2}\sum_{\substack{m_1n_1l_1\\ \mu_1\nu_1}}\beta_{\mu_1}\lambda^{m_1n_1l_1}_{\mu_1\nu_1}\sum_{\substack{m_2n_2l_2\\ \mu_2\nu_2}}[(2m_1+1)(2n_1+1)(2m_2+1)(2n_2+1)]^{1/2}$$
$$\times\begin{Bmatrix} m_1 & n_1 & l_1\\ m_2 & n_2 & l_2\\ m & n & l\end{Bmatrix}\begin{pmatrix} l_1 & l_2 & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} n_1 & n_2 & n\\ \nu_1 & \nu_2 & -\nu\end{pmatrix}\begin{pmatrix} m & m_1 & m_2\\ -\mu-\Delta_\beta & \mu_1+\Delta_\beta & \mu_2\end{pmatrix} i^{m_2n_2l_2}_{\mu_2\nu_2}(\boldsymbol{\lambda}), \tag{3.10}$$

where for

$$J_\beta = J_\pm\,\beta_\mu = [(m\pm\mu)(m\mp\mu+1)]^{1/2},$$
$$\Delta_\beta = \pm 1, \tag{3.11}$$

and for

$$J_\beta = J_0,\quad \beta_\mu = \mu,$$
$$\Delta_\beta = 0. \tag{3.12}$$

Similarly for the irreducible representation of the GBF we get the simpler recursion relation

$$\beta_\mu i^{mn}_{\mu_1\nu_1\chi}(\boldsymbol{\alpha}) = (-)^{\mu+\nu+1}[(2m+1)(2n+1)]^{1/2}\sum_{\substack{m_1n_1\\ \nu_1\mu_1\chi_1}}\alpha^{m_1n_1}_{\mu_1\nu_1\chi_1}\beta_{\mu_1}[(2m_1+1)(2n_1+1)(2m_2+1)(2n_2+1)]^{1/2}$$
$$\times\sum\begin{pmatrix} m_1 & m_2 & m\\ \chi_1 & \chi_2 & \chi\end{pmatrix}\begin{pmatrix} m_1 & m_2 & m\\ -\mu-\Delta & \mu_2 & \mu_1+\Delta\end{pmatrix}\begin{pmatrix} n & n_2 & n_1\\ -\nu & \nu_2 & \nu_1\end{pmatrix}\begin{pmatrix} n_1 & n_2 & n\\ -\chi_1 & -\chi_2 & -\chi\end{pmatrix} i^{m_2n_2}_{\mu_2\nu_2\chi_2}(\boldsymbol{\alpha}). \tag{3.13}$$

Equations (3.10) and (3.13) are generalizations of recursion relations for ordinary Bessel functions.

IV. THE DIPOLAR INTERACTION

Consider now the most general exponential for the dipole–dipole interaction or correlation. It is of the form

$$W(\boldsymbol{\lambda}) = \lambda_0\Phi^{110} + \lambda_2\Phi^{112}, \tag{4.1}$$
$$W(\boldsymbol{\alpha}) = \alpha_0\Phi^{11}_0 + \alpha_1(\Phi^{11}_1 + \Phi^{11}_{-1}). \tag{4.2}$$

Explicitly, from Eq. (2.2),

$$\Phi^{110} = -\sqrt{3}[\sin\theta_1\sin\theta_2\cos\phi_{12} + \cos\theta_1\cos\theta_2],$$
$$\Phi^{112} = \sqrt{3/10}[-\sin\theta_1\sin\theta_2\cos\phi_{12} + 2\cos\theta_1\cos\theta_2], \tag{4.3}$$

and

$$\Phi_0^{11} = 3\cos\theta_1 \cos\theta_2, \qquad (4.4)$$

$$\Phi_{\pm 1}^{11} = -3/2 \sin\theta_1 \sin\theta_2 \, e^{\pm i\varphi_{12}}$$

from where, using Eq. (2.8),

$$\alpha_0 = 1/\sqrt{3}(-\lambda_0 + 2/\sqrt{10}\lambda_2),$$

$$\alpha_1 = 1/\sqrt{3}(\lambda + 1/\sqrt{10}\lambda_2) \qquad (4.5)$$

which establishes the equivalence between the representations for this case. Consider now the irreducible representation (4.2). It is clear that the rotational invariants can be written as traces of tensorial operators.[11] In our simple case, the dipolar interaction term can be expressed in terms of two unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$ in a reference frame $(\mathbf{k}_x\mathbf{k}_y\mathbf{k}_z)$, where $\mathbf{k}_z$ points in the direction of $\mathbf{r}_{12}$. We define

$$\mathbf{k}_+ = -1/\sqrt{2}(\mathbf{k}_x + i\mathbf{k}_y),$$

$$\mathbf{k}_- = 1/\sqrt{2}(\mathbf{k}_x - i\mathbf{k}_y), \qquad (4.6)$$

then

$$\mathbf{e}_i\cdot\mathbf{k}_z = \cos\theta_i,$$

$$\mathbf{e}_i\cdot\mathbf{k}_\pm = \sin\theta_i \, e^{\pm i\varphi_i}, \quad i = 1,2. \qquad (4.7)$$

From Eq. (4.4),

$$\Phi_0^{11} = 3(\mathbf{e}_1\cdot\mathbf{k}_z)(\mathbf{e}_1\cdot\mathbf{k}_z) \qquad (4.8)$$

and

$$\Phi_{\pm 1}^{11} = 3(\mathbf{e}_1\cdot\mathbf{k}_\pm)(\mathbf{e}_1\cdot\mathbf{k}_\mp) \qquad (4.9)$$

from where we may write

$$W(\alpha) = \mathbf{e}_1\cdot\{3\alpha_0\mathbf{k}_z \cos\theta_2 - 3/\sqrt{2}\mathbf{k}_+\alpha_1 \sin\theta_2 \, e^{-i\varphi_2} - 3/\sqrt{2}\mathbf{k}_-\alpha_1 \sin\theta_2 \, e^{i\varphi_2}\} \qquad (4.10)$$

or

$$W(\alpha) = \mathbf{e}_1\cdot\mathbf{A}$$

with

$$\mathbf{A} = 3\alpha_0\mathbf{k}_z \cos\theta_2 - 3/\sqrt{2}\mathbf{k}_+\alpha_1 \sin\theta_2 \, e^{-i\varphi_2} - 3/\sqrt{2}\mathbf{k}_-\alpha_1 \sin\theta_2 \, e^{i\varphi_2}. \qquad (4.11)$$

From Eq. (2.12) we get the first member of the family

$$i_0^{00}(\alpha_0\alpha_1) = 1/16\pi^2 \int_{-1}^{1} d\cos\theta_1 \int_0^{2\pi} d\phi_1 \times \int_{-1}^{1} d\cos\theta_2 \int_0^{2\pi} d\phi_2 \, e^{-\mathbf{e}_1\cdot\mathbf{A}} = 1/4\pi \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi \, i_0(|\mathbf{A}|). \qquad (4.12)$$

Here $i_0(x) = \sinh(x)/x$ is the spherical modified Bessel function of zero order. Using Eq. (4.11),

$$i_0^{00}(\alpha_0\alpha_1) = 1/2 \int_{-1}^{1} d\cos\theta_2 \, i_0 \times (3[\alpha_1^2 + (\alpha_0^2 - \alpha_1^2)\cos^2\theta_2]^{1/2}) \qquad (4.13)$$

which is our main result. When $\alpha_0 = \alpha_1$ then we find the known result

$$i_0^{00}(\alpha_0,\alpha_0) = i_0(3\alpha_0) \qquad (4.14)$$

which is the first term in the expansion of

$$e^{-3\alpha_0[\Phi_0^{11} - (\Phi_1^{11} + \Phi_{-1}^{11})]} = e^{-3\alpha_0\mathbf{e}_1\cdot\mathbf{e}_2} = \sum_{l=0}^{\infty} (-)^l(2l+1) i_l(3\alpha_0) P_l(\mathbf{e}_1\cdot\mathbf{e}_2). \qquad (4.15)$$

Finally, using the recurrence relation (3.8) we get

$$i_0^{11} = \frac{\partial i^{00}(\alpha_0\alpha_1)}{\partial\alpha_0},$$

$$i_0^{11}(\alpha_0\alpha_1) = -3/2 \int_{-1}^{1} d\cos\theta_2 \times \frac{i_1(3[\alpha_1^2 + (\alpha_0^2 - \alpha_1^2)\cos^2\theta_2]^{1/2})\alpha_0\cos^2\theta_2}{\sqrt{\alpha_1^2 + (\alpha_0^2 - \alpha_1^2)\cos^2\theta_2}} \qquad (4.16)$$

and

$$i_{\pm 1}^{11} = \frac{(1/2)\partial i_0^{00}(\alpha_0\alpha_1)}{\partial\alpha_1},$$

$$i_{\pm 1}^{11}(\alpha_0\alpha_1) = -3/4 \int_{-1}^{1} d\cos\theta_2 \times \frac{i_1(3[\alpha_1^2 + (\alpha_0^2 - \alpha_1^2)\cos^2\theta_2]^{1/2})\alpha_1\sin^2\theta_2}{\sqrt{\alpha_1^2 + (\alpha_0^2 - \alpha_1^2)\cos^2\theta_2}}. \qquad (4.17)$$

The corresponding GBF for the invariant l representation can be obtained using the inverse of Eq. (2.13).

V. THE LINEAR QUADRUPOLE CASE

In recent work on the structure and thermodynamics of liquid water, a model of spheres with embedded dipoles and quadrupoles was used.[12] The interesting feature of this model is that it can be studied using integral equations for a variety of systems. Recently Perera *et al.*[13] have solved the HNC equation for this model. For simplicity, however, we will discuss the case of the linear quadrupole only. The treatment of the nonlinear quadrupole follows the same factorization method, but is more complicated.

In this case the exponent is of the form

$$W(\lambda) = \lambda_0\Phi^{220} + \lambda_2\Phi^{222} + \lambda_4{}^{224}. \qquad (5.1)$$

In the irreducible χ form this expression reads

$$W(\alpha) = \alpha_0\Phi_0^{22} + \alpha_1[\Phi_1^{22} + \Phi_{-1}^{22}] + \alpha_2[\Phi_2^{22} + \Phi_{-2}^{22}], \qquad (5.2)$$

where

$$\Phi_0^{22} = 5/4(3\cos^2\theta_1 - 1)(3\cos^2\theta_2 - 1), \qquad (5.3)$$

$$\Phi_{\pm 1}^{22} = -15/2 \sin\theta_1 \cos\theta_1 \sin\theta_2 \cos\theta_2 \, e^{\pm i\varphi_{12}}, \qquad (5.4)$$

$$\Phi_{\pm 2}^{22} = 15/8 \sin^2\theta_1 \sin^2\theta_2 \, e^{\pm 2i\varphi_{12}}. \qquad (5.5)$$

From Eq. (2.8) we get the relations

$$\alpha_0 = 1/\sqrt{5}\lambda_0 - \sqrt{2/35}(\lambda_2 - \lambda_4), \qquad (5.6)$$

$$\alpha_1 = -1/\sqrt{5}\lambda_0 + \sqrt{2/35}(\lambda_2/2 + 2\lambda_4/3), \qquad (5.7)$$

$$\alpha_2 = 1/\sqrt{5}\lambda_0 + \sqrt{2/35}(\lambda_2 + 2\lambda_4/6). \qquad (5.8)$$

In the tensorial representation we have, following the same method as in Sec. IV,

$$\Phi_0^{22} = 5/4 \mathsf{e}_1\mathsf{e}_1 : \{[3\mathsf{k}_z\mathsf{k}_z - \mathsf{I}](3\cos^2\theta_2 - 1)\}, \quad (5.9)$$

where $\mathsf{e}_1\mathsf{e}_1$ is a vector dyadic:

$$\Phi_{\pm 1}^{22} = 15/2 \mathsf{e}_1\mathsf{e}_1 : \{[\mathsf{k}_z\mathsf{k}_\pm](\sin\theta_2\cos\theta_2\, e^{i\varphi_2})\}, \quad (5.10)$$

$$\Phi_{\pm 2}^{22} = 15/4 \mathsf{e}_1\mathsf{e}_1 : \{[\mathsf{k}_\pm\mathsf{k}_\pm](\sin^2\theta_2\, e^{\pm 2i\varphi_2})\}. \quad (5.11)$$

From Eq. (5.2) we see that

$$W(\alpha) = \mathsf{e}_1 \cdot \mathsf{B} \cdot \mathsf{e}_1, \quad (5.12)$$

where B is a matrix that depends on the coordinates of two alone. Since $W(\alpha)$ is a function of $\phi_{12} = \phi_1 - \phi_2$ alone, we may choose $\phi_2 = 0$. Then

$$\mathsf{B} = 5/4 \begin{bmatrix} 3\alpha_2\sin^2\theta_2 - \alpha_0(3\cos^2\theta_2 - 1) & 0 & -6\alpha_1\cos\theta_2\sin\theta_2 \\ 0 & -3\alpha_2\sin^2\theta_2 - \alpha_0(3\cos^2\theta_2 - 1) & 0 \\ -6\alpha_1\cos\theta_2\sin\theta_2 & 0 & 2\alpha_0(3\cos^2\theta_2 - 1) \end{bmatrix}. \quad (5.13)$$

Since we need to integrate over all orientations of $\mathbf{e}$, we can pick a frame that diagonalizes B. Then

$$W(\alpha) = -5/4\{\zeta_1 x_1^2 + \zeta_2 y_1^2 + \zeta_3 z_1^2\}, \quad (5.14)$$

where

$$x_1 = \sin\theta_1\cos\phi_1,$$
$$y_1 = \sin\theta_1\sin\phi_1,$$
$$z_1 = \cos\theta_1. \quad (5.15)$$

It will be convenient to change variables to

$$r^2 = x_1^2 + y_1^2 + z_1^2 = 1,$$
$$u^2 = x_1^2 - y_1^2 = \sin^2\theta_1\cos 2\phi_1,$$
$$v^2 = -x_1^2 - y_1^2 + 2z_1^2 = 3\cos^2\theta_1 - 1 \quad (5.16)$$

so that

$$W(\alpha) = -5/24\{2r^2[\zeta_1 + \zeta_2 + \zeta_3] + 3u^2[\zeta_1 - \zeta_2] + v^2[2\zeta_3 - \zeta_1 - \zeta_2]\}, \quad (5.17)$$

and finally

$$W(\alpha) = -5/4\{\sqrt{D}\sin^2\theta_1\cos 2\phi_1 + 1/2\zeta_3(3\cos^2\theta_1 - 1)\}. \quad (5.18)$$

The eigenvalues of B, Eq. (5.13), are

$$\zeta_3 = -[2\alpha_0 - 3\sin^2\theta_2(\alpha_2 - \alpha_0)],$$
$$\zeta_2 = -[\zeta_3 + \sqrt{D}]/2,$$
$$\zeta_1 = -[\zeta_3 - \sqrt{D}]/2, \quad (5.19)$$

where

$$D = \zeta_3^2 - 4[2\zeta_3\alpha_0(2 - 3\sin^2\theta_2) - \alpha_1\sin^2\theta_2\cos^2\theta_2]. \quad (5.20)$$

The result for the first member of the GBF for the linear quadrupole is then

$$i_0^{00}(\alpha) = 1/4\int_{-1}^{1} d\cos\theta_1 \int_{-1}^{1} d\cos\theta_2\, e^{-5/8\zeta_3(3\cos^2\theta_1 - 1)} \times I_0[5/8\sqrt{D}\sin^2\theta_1], \quad (5.21)$$

where $I_0(x)$ is the modified cylindrical Bessel function.

VI. CONCLUSIONS

In this work we introduce the GBF and discuss some elementary properties of these complicated functions. The integral representation should be useful in computing numerically the GBFs. In the case of linear multipoles the integrations are at most three dimensional and in the cases discussed in Secs. IV and V, we have shown that they can be reduced to one and two dimensional integrals. The factorization method used in these sections can, in principle, be extended to nonlinear multipoles. This point, and also the formulation of series, Pade, continued fractions and other useful approximation is left for future work.

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