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Some remarks on generalised multipole expansions

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Abstract. Models for the mutual potential energy between two molecules proposed in the scientific literature often contain a sum of inverse-power interactions involving pairs of sites belonging to the two particles; in turn, these quantities are functions of a few scalar invariants involved in the problem at hand, and one is often interested in directly obtaining an explicit expression of the potential in terms of the latter; the extensively studied two-centre multipole expansion for the mutual electrostatic energy between two charge distributions is a well-known example of this procedure and of its restrictions. We consider here another, less widely known and possibly complementary, approach, proposed by Šebek some years ago [J. Šebek, Czech. J. Phys. B **38**, 1185 (1988)]; the resulting formulae show that this procedure can become computationally favourable for sufficiently high molecular symmetry.

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1 Introduction

Models for the mutual potential energy between two molecules proposed in the scientific literature [1–4] often contain a sum of inverse-power interactions involving pairs of sites belonging to the two particles; in turn, these quantities are functions of a few scalar invariants involved in the problem at hand, and one is often interested in directly obtaining an explicit expression of the potential in terms of these invariants; the extensively studied two-centre multipole expansion for the mutual electrostatic energy between two charge distributions is a well-known example of this procedure and of its restrictions (see, for example, Refs. [4,5]). The present paper addresses another, less widely known and possibly complementary, approach [6].

To be more specific, let P, A, B, Q (in this order), denote any four distinct points in ordinary three-dimensional Euclidean space, and let $\mathbf{x}_P$, $\mathbf{x}_A$, $\mathbf{x}_B$, $\mathbf{x}_Q$ denote their coordinate vectors with respect to a common arbitrary Cartesian frame, defined by an orthonormal triad $\{\mathbf{e}_l\}$; A and B will eventually be interpreted as molecular centres, P and Q as interaction sites. Thus

$$\mathbf{x}_Q - \mathbf{x}_P = (\mathbf{x}_Q - \mathbf{x}_B) + (\mathbf{x}_B - \mathbf{x}_A) - (\mathbf{x}_P - \mathbf{x}_A), \quad (1)$$

which gives rise to the corresponding expression for $|\mathbf{x}_Q - \mathbf{x}_P|^2$; it will prove notationally convenient to define

$$\mathbf{a} = \mathbf{x}_P - \mathbf{x}_A, \quad \mathbf{b} = \mathbf{x}_Q - \mathbf{x}_B, \quad \mathbf{R} = \mathbf{x}_B - \mathbf{x}_A, \quad (2)$$

$$a = |\mathbf{a}|, \quad b = |\mathbf{b}|, \quad R = |\mathbf{R}|, \quad \mathbf{r} = \mathbf{R}/R, \quad (3)$$

thus

$$|\mathbf{x}_Q - \mathbf{x}_P|^2 = R^2 + a^2 + b^2 + \eta, \quad (4)$$

where

$$\eta = 2\left[(\mathbf{b}\cdot\mathbf{R}) - (\mathbf{a}\cdot\mathbf{R}) - (\mathbf{a}\cdot\mathbf{b})\right]. \quad (5)$$

Let us now consider the quantity

$$\Phi_\alpha = |\mathbf{x}_Q - \mathbf{x}_P|^\alpha, \quad (6)$$

where α denotes an arbitrary real number; when α is an even positive integer, Φ_α is just a polynomial in the appropriate scalar products; otherwise, under additional conditions, it can be expanded in an infinite series; notice that equation (6) can be rewritten

$$\Phi_\alpha = R^\alpha(1+\zeta)^\beta, \ \zeta = (\eta + a^2 + b^2)/R^2, \quad (7)$$

where $\beta = \alpha/2$; Φ_α can also be rewritten as [6]

$$\Phi_\alpha = \rho^\beta(1+\xi)^\beta, \ \rho = (R^2 + a^2 + b^2), \ \xi = \eta/\rho. \quad (8)$$

The multipolar expansion ($\alpha = -1$) and its extensions to other values of α [5,10–14] (hereinafter referred to as ME)

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are based on a series expansion of equation (7) in powers of ζ, under the condition $R > (a+b)$; a general reformulation of this treatment can be found in reference [15]; on the other hand, an expansion of equation (8) in powers of ξ (hereinafter referred to as SE) was proposed by Šebek some years ago [6], and applied by the same author in connection with mesogenic potential models [7–9]; the condition for convergence, $\xi < 1$, is satisfied as long as the four points are distinct [6]. In other words, there exists a close range of mutual distances and orientations where ME of equation (7) diverges, whereas SE of equation (8) remains convergent; both expansions converge over the more distant range, and the latter has a better convergence than the former [6,16]; a precedent of this idea can be traced back to reference [17].

Let us now consider two sets of interacting points $\{P_j,\ j = 1, 2, \dots M\}$ and $\{Q_k,\ k = 1, 2, \dots N\}$, arbitrarily distributed around the two molecular centres A and B, respectively; let

$$\begin{aligned} \mathbf{p}_j &= \mathbf{x}_{P_j} - \mathbf{x}_A, \quad j = 1, 2, \dots M, \\ \mathbf{q}_k &= \mathbf{x}_{Q_k} - \mathbf{x}_B, \quad k = 1, 2, \dots N, \end{aligned} \tag{9}$$

$$p_j = |\mathbf{p}_j|,\ q_k = |\mathbf{q}_k|,\ a = \max(p_j),\ b = \max(q_k); \tag{10}$$

quantities $\xi_{jk},\ \eta_{jk},\ \zeta_{jk}$ can be defined by appropriate generalisations of the above $\xi,\ \eta,\ \zeta$, respectively (Eqs. (4–8)); Φ_α is now generalised to

$$\Psi_\alpha = \sum_{j=1}^{M} \sum_{k=1}^{N} C_{jk} |\mathbf{x}_{P_j} - \mathbf{x}_{Q_k}|^\alpha. \tag{11}$$

When $R > (a+b)$, usage of ME in equation (7) makes it possible to factor out powers of R, whose coefficients are given by contracted products between appropriate interaction and multipole tensors, respectively (see, for example, Ref. [4]); in turn, these tensors can be constructed in two equivalent ways, i.e. in terms of Cartesian or spherical components; an alternative, computationally more efficient, approach has been studied in reference [15]. On the other hand, usage of SE (Eq. (8)) yields a better convergence, but, in principle, it leads to (MN) different infinite series, one for for each power in equation (11). There still exist some computationally favourable cases, of sufficiently high symmetry, i.e. when all quantities p_j have a common value a, and all quantities q_k have a common value b, so that the (MN) infinite series can be collapsed into one. In these cases one obtains a result of the form

$$\begin{aligned} \Psi_\alpha &= \rho^\beta \\ &\times \left[\sigma_0 + \beta\sigma_1 + \frac{\beta(\beta-1)}{2!}\sigma_2 + \frac{\beta(\beta-1)(\beta-2)}{3!}\sigma_3 + \dots \right], \end{aligned} \tag{12}$$

where

$$\sigma_L = \sum_{j=1}^{M} \sum_{k=1}^{N} C_{jk} \xi_{jk}^L = \tau_L / \rho^L, \quad \tau_L = \sum_{j=1}^{M} \sum_{k=1}^{N} C_{jk} \eta_{jk}^L; \tag{13}$$

this expansion converges, in general, as long as all the interacting sites remain distinct, and hence, in particular, when $R > (a+b)$; each term σ_L is independent of α, and some of them may vanish by symmetry; if the quantities C_{jk} have a nontrivial common divisor $\overline{C}$ (e.g. a common value, or a common absolute value), this can be conveniently factored out. When both $M \le 2$ and $N \le 2$, no more than four interacting points are involved, and neither expansion appears to offer any significant computational advantage over the straightforward evaluation of the appropriate powers.

As for notation, coordinates of the interacting sites in the two extended molecules, i.e. the vectors $\mathbf{p}_j$ and $\mathbf{q}_k$, will be expressed in terms of two sets of orthonormal vectors $\{\mathbf{u}_\iota,\ \iota = 1, 2, 3\}$ and $\{\mathbf{v}_\kappa,\ \kappa = 1, 2, 3\}$ defining molecular orientations (for example as defined by the eigenvectors of the two inertia tensors); let us thus define

$$\mathcal{P} \equiv \{R,\ a,\ b\}, \tag{14}$$

$$\mathcal{O} \equiv \{\lambda_\iota,\ \mu_\kappa,\ \nu_{\iota\kappa},\ \iota, \kappa = 1, 2, 3\}, \tag{15}$$

$$\lambda_\iota = \mathbf{u}_\iota \cdot \mathbf{r},\ \mu_\kappa = \mathbf{v}_\kappa \cdot \mathbf{r},\ \nu_{\iota\kappa} = \mathbf{u}_\iota \cdot \mathbf{v}_\kappa. \tag{16}$$

As for the general structure of equation (12), each term σ_L is a linear combination of products of rational functions of $\mathcal{P}$ (radial functions, for short), multiplied by polynomials in $\mathcal{O}$ (angular functions for short); each angular function, in turn, can be re-expressed by a linear combination of $S-$functions (see, e.g., chapter 3 in Ref. [4], or Refs. [18–20]). On the other hand, radial expansion coefficients of equation (11) with respect to the $S-$function basis can be obtained directly [12,14], possibly at the cost of determining them in a purely numerical way; a similar approach was used by Šebek in references [7–9].

Coefficients of the SE up to at least τ_3 will be presented in the following, for some simple cases involving identical interacting sites in two identical molecules; here the common value of a and b shall be denoted by d; numerical comparisons and a more extensive tabulation can be found in reference [16]; the needed algebraic manipulations were carried out by means of the packages Derive and Maple.

2 Discrete interaction sites

2.1 Regular polygons

In the case of two identical regular polygons of N vertices, coordinates of the interacting sites (Eq. (9)) are given by

$$\begin{aligned} \mathbf{p}_j &= d\left(\cos\chi_j \mathbf{u}_1 + \sin\chi_j \mathbf{u}_2\right), \\ \mathbf{q}_k &= d\left(\cos\upsilon_k \mathbf{v}_1 + \sin\upsilon_k \mathbf{v}_2\right), \end{aligned} \tag{17}$$

where

$$\chi_j = 2\pi(j/N),\ \upsilon_k = 2\pi(k/N), \quad j, k = 1, 2, \dots, N; \tag{18}$$

here the two unit vectors $\mathbf{u}_3$ and $\mathbf{v}_3$, respectively, have been chosen to be orthogonal to the polygon planes; the expansion coefficients can be worked out for generic N as well, and are given by

$$\tau_0 = N^2 \tag{19}$$

$$\tau_1 = 0 \tag{20}$$

$$\begin{aligned}\tau_2 &= N^2\ d^2\ \left[d^2 \sum_{\iota=1}^{2}\sum_{\kappa=1}^{2} \nu_{\iota\kappa}^2 + 2R^2 \sum_{\iota=1}^{2}\left(\lambda_\iota^2 + \mu_\iota^2\right)\right] \\ &= N^2\ d^2\ \left[d^2\left(1+\nu_{33}^2\right) + 2R^2\left(2-\lambda_3^2-\mu_3^2\right)\right]\end{aligned} \tag{21}$$

$$\tau_3 = 12N^2\ d^4\ R^2\ \sum_{\iota=1}^{2}\sum_{\kappa=1}^{2} \lambda_\iota \nu_{\iota\kappa}\mu_\kappa \tag{22}$$

$$\tau_4 = N^2\ d^4\ \left(6F_1 + 6d^2R^2F_2 + d^4R^4F_3\right) \tag{23}$$

where

$$\begin{aligned}F_1 &= \sum_{\iota=1}^{2}\left(\lambda_\iota^4 + \mu_\iota^4\right) + 2\left(\lambda_1^2\lambda_2^2 + \mu_1^2\mu_2^2\right) \\ &\quad + 4\left(\sum_{\iota=1}^{2}\lambda_\iota^2\right)\left(\sum_{\kappa=1}^{2}\mu_\kappa^2\right)\end{aligned} \tag{24}$$

$$\begin{aligned}F_2 &= 4\left[\lambda_1\lambda_2\left(\nu_{11}\nu_{21}+\nu_{12}\nu_{22}\right) + \mu_1\mu_2\left(\nu_{11}\nu_{12}+\nu_{21}\nu_{22}\right)\right] \\ &\quad + \left(\lambda_1^2+\mu_1^2\right)\nu_{22}^2 + \left(\lambda_2^2+\mu_2^2\right)\nu_{11}^2 \\ &\quad + 3\left(\lambda_1^2+\mu_1^2\right)\nu_{11}^2 + 3\left(\lambda_2^2+\mu_2^2\right)\nu_{22}^2 \\ &\quad + \left(\lambda_1^2+\mu_2^2\right)\left(3\nu_{12}^2+\nu_{21}^2\right) + \left(\lambda_2^2+\mu_1^2\right)\left(3\nu_{21}^2+\nu_{12}^2\right)\end{aligned} \tag{25}$$

$$\begin{aligned}F_3 &= +(9/4)\left(\nu_{11}^4+\nu_{12}^4+\nu_{21}^4+\nu_{22}^4\right) \\ &\quad + (9/2)\left(\nu_{12}^2+\nu_{21}^2\right)\left(\nu_{11}^2+\nu_{22}^2.\right) \\ &\quad + (3/2)\left(\nu_{11}^2\nu_{22}^2+\nu_{12}^2\nu_{21}^2\right) + 6\nu_{11}\nu_{12}\nu_{21}\nu_{22}.\end{aligned} \tag{26}$$

2.2 Cube, tetrahedron, octahedron

In working out results for these polyhedra, it proves convenient to start from a cube with edge length 2Δ, and to consider the other two figures as suitably inscribed in it, i.e. the vertices of the octahedron occupy centres of cube faces, and vertices of the tetrahedron occupy every other vertex of the cube.

For the octahedron, $\Delta = d$, $\rho = R^2 + 2d^2$, and results read

$$\tau_0 = 36 \tag{27}$$

$$\tau_1 = 0 \tag{28}$$

$$\begin{aligned}\tau_2 &= 16\ \left[3d^2R^2\sum_{\iota=1}^{3}\left(\lambda_\iota^2+\mu_\iota^2\right) + d^4\sum_{\iota=1}^{3}\sum_{\kappa=1}^{3}\nu_{\iota\kappa}^2\right] \\ &= 48\ d^2\ \left(2R^2+d^2\right)\end{aligned} \tag{29}$$

$$\tau_3 = 192\ d^4\ R^2\ \sum_{\iota=1}^{3}\sum_{\kappa=1}^{3}\lambda_\iota\nu_{\iota\kappa}\mu_\kappa \tag{30}$$

$$\begin{aligned}\tau_4 &= 16\left[12d^4R^4\left(\sum_{\iota=1}^{3}\lambda_\iota^4 + \sum_{\kappa=1}^{3}\mu_\kappa^4 + 2\right)\right. \\ &\quad \left. +24d^6R^2\sum_{\iota=1}^{3}\sum_{\kappa=1}^{3}(\lambda_\iota^2+\mu_\kappa^2)\nu_{\iota\kappa}^2 + 4d^8\sum_{\iota=1}^{3}\sum_{\kappa=1}^{3}\nu_{\iota\kappa}^4\right]\end{aligned} \tag{31}$$

$$\begin{aligned}\tau_5 &= 2560\left\{d^6R^4\sum_{\iota=1}^{3}\sum_{\kappa=1}^{3}\left[\lambda_\iota\mu_\kappa\left(\lambda_\iota^2+\mu_\kappa^2\right)\nu_{\iota\kappa}\right]\right. \\ &\quad \left. +d^8R^2\sum_{\iota=1}^{3}\sum_{\kappa=1}^{3}\lambda_\iota\mu_\kappa\nu_{\iota\kappa}^3\right\}.\end{aligned} \tag{32}$$

For both cube and tetrahedron, $\rho = R^2 + 6\Delta^2$; results for the cube read

$$\tau_0 = 64 \tag{33}$$

$$\tau_1 = 0 \tag{34}$$

$$\tau_2 = 256\ \Delta^2\ \left(2R^2+3\Delta^2\right) \tag{35}$$

$$\tau_3 = 3072\ \Delta^4\ R^2\ \sum_{\iota=1}^{3}\sum_{\kappa=1}^{3}\lambda_\iota\nu_{\iota\kappa}\mu_\kappa. \tag{36}$$

$$\tau_4 = 1024\ \left(b_4\Delta^4R^4 + b_6\Delta^6R^2 + b_8\Delta^8\right), \tag{37}$$

where

$$b_4 = 12 - 2\sum_{\iota=1}^{3}\lambda_\iota^4 - 2\sum_{\kappa=1}^{3}\mu_\kappa^4 \tag{38}$$

$$b_6 = 36 + 24\sum_{\iota=1}^{3}\sum_{\kappa\neq\iota}\sum_{l=1}^{3}\left(\lambda_\iota\lambda_\kappa\nu_{\iota l}\nu_{\kappa l} + \mu_\iota\mu_\kappa\nu_{l\iota}\nu_{l\kappa}\right) \tag{39}$$

$$b_8 = 27 - 2\sum_{\iota=1}^{3}\sum_{\kappa=1}^{3}\nu_{\iota\kappa}^4 + 24c_8 \tag{40}$$

$$\begin{aligned}c_8 &= \nu_{32}\nu_{33}\nu_{12}\nu_{13} + \nu_{21}\nu_{31}\nu_{33}\nu_{23} + \nu_{22}\nu_{32}\nu_{33}\nu_{23} \\ &\quad + \nu_{13}\nu_{21}\nu_{11}\nu_{23} + \nu_{21}\nu_{22}\nu_{12}\nu_{11} + \nu_{11}\nu_{32}\nu_{31}\nu_{12} \\ &\quad + \nu_{11}\nu_{33}\nu_{31}\nu_{13} + \nu_{31}\nu_{32}\nu_{22}\nu_{21} + \nu_{22}\nu_{23}\nu_{12}\nu_{13}.\end{aligned} \tag{41}$$

For the tetrahedron:

$$\tau_0 = 16 \tag{42}$$

$$\tau_1 = 0 \tag{43}$$

$$\tau_2 = 64\ \Delta^2\ \left(2R^2+3\Delta^2\right) \tag{44}$$

$$\tau_3 = 768\ \Delta^3\ \left(R^3F_1 + \Delta R^2F_2 + \Delta^2RF_3 - \Delta^3F_4\right) \tag{45}$$

where

$$F_1 = (\mu_1\mu_2\mu_3 - \lambda_1\lambda_2\lambda_3) \tag{46}$$

$$F_2 = \sum_{\iota=1}^{3}\sum_{\kappa=1}^{3} \lambda_\iota \nu_{\iota\kappa} \mu_\kappa \tag{47}$$

$$\begin{aligned} F_3 = &+\nu_{11}\left(\mu_2\nu_{13} + \mu_3\nu_{12} - \lambda_2\nu_{31} - \lambda_3\nu_{21}\right) \\ &+ \nu_{22}\left(\mu_1\nu_{23} + \mu_3\nu_{21} - \lambda_1\nu_{32} - \lambda_3\nu_{12}\right) \\ &+ \nu_{33}\left(\mu_1\nu_{32} + \mu_2\nu_{31} - \lambda_1\nu_{23} - \lambda_2\nu_{13}\right) \\ &+ \left(\mu_1\nu_{12}\nu_{13} + \mu_2\nu_{21}\nu_{23} + \mu_3\nu_{31}\nu_{32}\right. \\ &\left.-\lambda_1\nu_{21}\nu_{31} - \lambda_2\nu_{12}\nu_{32} - \lambda_3\nu_{13}\nu_{23}\right) \end{aligned} \tag{48}$$

$$\begin{aligned} F_4 = &+\nu_{11}\nu_{22}\nu_{33} + \nu_{11}\nu_{23}\nu_{32} + \nu_{12}\nu_{21}\nu_{33} \\ &+ \nu_{12}\nu_{23}\nu_{31} + \nu_{13}\nu_{21}\nu_{32} + \nu_{13}\nu_{22}\nu_{31}. \end{aligned} \tag{49}$$

3 Continuous distributions of interaction sites

3.1 Rings in 3 – d space

The above treatment can also be applied to uniform continuous distributions of interaction centres, so that the sums appearing in equation (13) are replaced by appropriate integrals; for example, for two circular distributions (rings in $3-d$ space), equation (17) is modified to

$$\mathbf{p} = d\left(\cos\phi_1\mathbf{u}_1 + \sin\phi_1\mathbf{u}_2\right), \ \mathbf{q} = d\left(\cos\phi_2\mathbf{v}_1 + \sin\phi_2\mathbf{v}_2\right); \tag{50}$$

after some algebra, results can be expressed in terms of the three relevant scalar products λ_3, μ_3, ν_{33}, i.e.

$$\tau_0 = 4\ \pi^2 \tag{51}$$

$$\tau_1 = 0 \tag{52}$$

$$\tau_2 = 4\ \pi^2\ d^2\ \left[d^2\left(1+\nu_{33}^2\right) + 2R^2\left(2-\lambda_3^2-\mu_3^2\right)\right] \tag{53}$$

$$\tau_3 = 48\ \pi^2\ d^4\ R^2\ \left(1-\lambda_3^2-\mu_3^2+\lambda_3\mu_3\nu_{33}\right) \tag{54}$$

$$\begin{aligned} \tau_4 = &+24\ \pi^2\ d^4\ R^4 \\ &\times\left[\left(2-\lambda_3^2-\mu_3^2\right)^2 + 2\left(1-\lambda_3^2\right)\left(1-\mu_3^2\right)\right] \\ &+ 48\ \pi^2\ d^6\ R^2 \\ &\times\left[2-2\lambda_3^2-2\mu_3^2-\left(\lambda_3^2+\mu_3^2\right)\nu_{33}^2+4\lambda_3\mu_3\nu_{33}\right] \\ &+ 24\ \pi^2\ d^6\ R^2\ \left(2-\lambda_3^2-\mu_3^2\right)\left(1+\nu_{33}^2\right). \end{aligned} \tag{55}$$

Elimination of other scalar products is accomplished by recalling that, for any two vectors $\mathbf{a}$, $\mathbf{b}$, and for any orthonormal triad $\{\mathbf{f}_l\}$,

$$\sum_{l=1}^{2}(\mathbf{a}\cdot\mathbf{f}_l)(\mathbf{b}\cdot\mathbf{f}_l) = (\mathbf{a}\cdot\mathbf{b}) - (\mathbf{a}\cdot\mathbf{f}_3)(\mathbf{b}\cdot\mathbf{f}_3), \tag{56}$$

and repeatedly applying this identity.

3.2 Coplanar rings and spherical shells

The above treatment can be applied to these cases as well, both involving a function of just one independent variable (R): here some exact solutions are available (see below), and other numerical strategies (such as tabulation of results obtained by numerical integration and subsequent interpolation) may become preferable.

In the first case the common plane is identified with the coordinate (x, y) plane, and $\mathbf{r}$ can be taken to define a coordinate axis, say $\mathbf{R} = R\mathbf{e}_1$, thus

$$\mathbf{p} = d\left(\cos\phi_1\mathbf{e}_1 + \sin\phi_1\mathbf{e}_2\right), \ \mathbf{q} = d\left(\cos\phi_2\mathbf{e}_1 + \sin\phi_2\mathbf{e}_2\right); \tag{57}$$

the resulting formulae read

$$\tau_0 = 4\ \pi^2 \tag{58}$$

$$\tau_1 = 0 \tag{59}$$

$$\tau_2 = 8\ \pi^2\ d^2\ \left(2R^2 + d^2\right) \tag{60}$$

$$\tau_3 = 48\ \pi^2\ d^4\ R^2 \tag{61}$$

$$\tau_4 = 24\ \pi^2\ d^4\ \left(d^4 + 8d^2R^2 + 6R^4\right). \tag{62}$$

These expressions can also be obtained as a special case of the previous ones, by setting $\lambda_3 = \mu_3 = 0,\ \nu_{33} = \pm 1$.

Notice also that, for $\alpha = -n$, where n denotes an even positive integer, integration with respect to the first angle can be carried out by the method of residues [21]; for $\alpha = -2$ or $\alpha = -4$, integration over the second angle can be carried out in closed form as well, yielding

$$\Psi_{-2} = 4\pi^2 d^2 \frac{1}{R\sqrt{R^2 - 4d^2}}, \tag{63}$$

$$\Psi_{-4} = 4\pi^2 d^4 \frac{\left(R^4 - 2d^2R^2 + 4d^4\right)}{R^3(R^2-4d^2)^2\sqrt{R^2-4d^2}}. \tag{64}$$

In the case of spherical shells, coordinates of the interacting sites are parameterised by

$$\begin{aligned} \mathbf{p} &= d\left(\sin\theta_1\cos\phi_1\mathbf{e}_1 + \sin\theta_1\sin\phi_1\mathbf{e}_2 + \cos\theta_1\mathbf{e}_3\right), \\ \mathbf{q} &= d\left(\sin\theta_2\cos\phi_2\mathbf{e}_1 + \sin\theta_2\sin\phi_2\mathbf{e}_2 + \cos\theta_2\mathbf{e}_3\right), \end{aligned} \tag{65}$$

and, without any loss of generality, $\mathbf{R} = R\mathbf{e}_3$; the resulting formulae read

$$\tau_0 = 16\ \pi^2 \tag{66}$$

$$\tau_1 = 0 \tag{67}$$

$$\tau_2 = \frac{64}{3}\ \pi^2\ d^2\ \left(d^2 + 2R^2\right) \tag{68}$$

$$\tau_3 = \frac{256}{3}\ \pi^2\ d^4\ R^2 \tag{69}$$

$$\tau_4 = \frac{256}{15}\ \pi^2\ d^4\ \left(3d^4 + 20d^2R^2 + 16R^4\right). \tag{70}$$

Notice in this context the exact result reported by Girifalco [22]:

$$\begin{aligned} \int d\omega_1 d\omega_2 |\mathbf{x}_Q - \mathbf{x}_P|^{-n} = &\frac{4\pi^2}{d^2(n-2)(n-3)} \\ &\times\left\{\frac{1}{R}\left[\frac{1}{(R-2d)^{(n-3)}} + \frac{1}{(R+2d)^{(n-3)}}\right] + \frac{2}{R^{(n-2)}}\right\}, \end{aligned} \tag{71}$$

where $n > 4$ is a positive integer, and $\int d\omega_1 d\omega_2$ denotes integration over the two spherical surfaces.

4 Conclusions

In the present paper we have revisited an alternative to ME for general inverse-power interactions, originally proposed by Šebek [6–9]; we have taken the two molecules to possess M and N interacting sites, respectively, and considered the special case where the M sites are all placed at a common distance a around the first molecular centre, and similarly the other N sites are placed at a common distance b around the second molecular centre. This comparatively high symmetry plays an important rôle, making it possible to collapse MN series into just one, whose coefficients can be evaluated in closed form, at least up to some order; formulae have been worked out in detail for some further simplified cases involving identical interaction sites in two identical molecules, thus $a = b$ and $M = N$. The above results suggest that this approach becomes computationally convenient as the number of interacting sites increases, or, even better, for continuous distributions of interacting centres, e.g. rings in $3-d$ space (in which case the interaction energy, resulting from numerical integration over two angles, is a function of seven independent variables). Let us mention in closing that references [7–9] dealt with mesogenic molecules: the above formulae for rings in $3-d$ space may be a useful starting point for simplified potential models of disk-like mesogenic molecules.

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