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Recurrence relations for the direct calculation of spherical multipole interaction tensors and Coulomb-type interaction energies

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Abstract

Recurrence relations for orientation-dependent multipole interaction tensors are derived in the spherical double-tensor formalism. These relations make it possible to calculate all interaction double-tensor components through order L in an expansion in $1/R$ with computational expenditures that scale as L^4. In contrast to Cartesian tensors, the orientation-dependent spherical double-tensors make it possible to evaluate electrostatic and induction energies with algorithms scaling as L^4. By introducing an intermediate transformation to a special coordinate system the matrix of spherical interaction tensor elements can be factorized into a product of three sparse matrices, each of which can be calculated within L^3 steps. We thus devise algorithms for the electrostatic, induction and dispersion energies that scale through order L in the multipole expansion as L^3, L^4 and L^5, respectively.

1. Introduction

The approximate calculation of the classical or coulomb part of the electrostatic interaction via multipole expansions plays an important role in many areas of computational chemistry such as molecular mechanics, potential theory and quantum chemistry. In the construction of Van der Waals potentials for weak intermolecular interactions multipole expansions are often used to obtain analytical expressions for the long range part of the electrostatic, induction and dispersion energy [1]. In Refs. [2-5] multipole approximations have been used to accelerate the assembly of the Coulomb matrix in quantum chemical calculations on large molecules.

Although the basic mathematical apparatus involved in the evaluation of multipole expansions has been well-known for several years [6-8] higher order multipole approximations are used only seldom. This is probably due to the fact that general expressions for the multipole interaction tensors, as deduced for example by Cipriani and Silvi [9] for the Cartesian multipole expansion or by Tough and Stone [10,11] for the spherical multipole expansion, are complicated in implementation and costly, scaling as L^6, where L is the order of the multipole expansion in $1/R$. In most applications, especially in molecular mechanics and in the simulation of molecular crystals, only the first few terms of the expansion (charge-charge, charge-dipole and dipole-dipole) are retained using explicit formulae for the components of the interaction tensors. Such formulae are easily derived for the Cartesian representation and for multipole moments given in a common global coordinate system. For the

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orientation-dependent spherical interaction tensors, explicit formulae up to fifth order in $1/R$ have been derived by Stone and coworkers [11–13], expressions up to sixth order can be found in Ref. [14].

However, for higher order multipole approximations it is more convenient to use recurrence relations that generate the higher-rank interaction tensors from the lower-rank ones, to obtain an efficient implementation of an open ended algorithm. Challacombe et al. [15] have derived such recurrence relations for the Cartesian multipole interaction tensors. The expressions given by these authors allow the calculation of all interaction tensors up to rank L by an algorithm that scales as L^4. However in a Cartesian multipole expansion there are $(L+1)(L+2)(L+3)/6$ moments at each expansion center; thus the calculation of electrostatic interaction energies via the bilinear product $\mathbf{Q}\cdot\mathbf{T}\cdot\mathbf{Q}$ still scales as L^6. Recently, we worked out an open ended algorithm, based on a derivation of orientation-dependent multipole interaction tensors given in Ref. [14] and a hybrid formalism between Cartesian and spherical multipole expansions [16]. Other hybrid methods have been proposed by Hinsen and Felderhof [17] employing compression matrices and by Panas [18] using coupling tensors. However, owing to the transformations between the Cartesian and spherical representations these algorithms do not perform better than the pure Cartesian expressions of Challacombe et al. [15]. In particular, the evaluation of the electrostatic interaction energies through order L in $1/R$ still needs $O(L^6)$ cpu time. Recently, Schulz [19] published recurrence relations for electrostatic interaction energy calculations using a complex spherical representation which reduces the scaling of the computational expenditure from $O(L^6)$ to $O(L^4)$. However, these recurrence relations are restricted to the case where the multipole moments at both centers are given in a common global coordinate system. This is naturally the case if the multipole expansion is used to speed up the evaluation of coulomb matrix elements in quantum chemical ab initio codes, but not for the computation of intermolecular interaction energies, where the multipole moments and the multipole-multipole polarizabilities are usually given in different molecule-fixed coordinate frames of the interacting components.

In this letter we derive recurrence relations for orientation-dependent spherical interaction tensors. Using spherical tensor techniques, we obtain expressions that allow the determination of all interaction tensor components through order L within a number of steps that scales as L^4. Unlike a Cartesian multipole expansion, in the spherical representation only $(L+1)^2$ multipole moments need be considered at each expansion center, so the derived recurrence relations enable the evaluation of electrostatic interaction energies through order L in $1/R$ within $O(L^4)$ cpu time. Because the orientation-dependence is included in the interaction double-tensors, no additional transformation of multipole moments, initially given in the molecule-fixed frames, to a global coordinate system is required in this formalism.

In Section 4 we show that when the interaction tensors are not needed explicitly but only in matrix–vector or matrix–matrix products of the type $\boldsymbol{T}\cdot\boldsymbol{Q}$ and $\boldsymbol{T}\cdot\boldsymbol{\alpha}$, where $\boldsymbol{Q}$ are multipole moments and $\boldsymbol{\alpha}$ multipole–multipole polarizabilities, it is favourable to introduce an intermediate transformation to a coordinate system with the z-axes parallel to the intermolecular distance vector. Thereby the matrix of orientation-dependent spherical interaction tensors is factorized into a product of three sparse matrices, each of which can be computed with $O(L^3)$ operations. In section 5 we employ this factorization to devise new algorithms for the computation of electrostatic, induction and dispersion energies using a real spherical multipole expansion, for which the computational costs scale through order L in the multipole expansion only as L^3, L^4 and L^5, respectively. Special attention has been paid to the point that the equations derived are as general as possible, so that they can be used with general unsymmetrical molecules and also with distributed multipole expansions, as needed for the computation of reliable interaction energies for assemblies with large non-spherical molecules.

2. Recurrence relations for complex spherical interaction tensors

The orientation- or angular-dependence of the interaction energy between two general molecules can be expanded in terms of the so-called S functions, which are defined as linear combinations of Wigner rotation matrices [10,11,20]:

$$S^{k_a k_b}_{l_a l_b j} = \mathrm{i}^{l_a - l_b - j} \sum_{m_a m_b m} D^{(l_a)}_{m_a k_a}(\Omega_a)^* D^{(l_b)}_{m_b k_b}(\Omega_b)^* D^{(j)}_{m0}(\Omega_{ab})^* \begin{pmatrix} l_a & l_b & j \\ m_a & m_b & m \end{pmatrix}, \tag{1}$$

where $\Omega_a = (\phi_a, \theta_a, \psi_a)$, $\Omega_b = (\phi_b, \theta_b, \psi_b)$ and $\Omega_{ab} = (\phi_{ab}, \theta_{ab})$ are Euler angles describing the orientation of the two molecule-fixed coordinate systems and the intermolecular distance vector, respectively. The expression in parentheses is a Wigner $3j$ symbol [21]. As has been shown by Tough and Stone [10,11], the complex spherical multipole interaction tensors are closely related to the subset of the S functions with $j = l_a + l_b$:

$$T^{(l_a,l_b)}_{k_a,k_b} = \frac{1}{4\pi\epsilon_0} R^{-l_a-l_b-1} \begin{pmatrix} l_a + l_b \\ l_a \end{pmatrix} \begin{pmatrix} l_a & l_b & l_a + l_b \\ 0 & 0 & 0 \end{pmatrix}^{-1} S^{k_a k_b}_{l_a l_b l_a + l_b}. \tag{2}$$

Because the S functions form a complete set, any product of two of them can be expressed as a linear combination of S functions, using the analogous expansion for products of Wigner rotation matrices [10,12]:

$$S^{k'_a k'_b}_{l'_a l'_b j'} \cdot S^{k''_a k''_b}_{l''_a l''_b j''} = \sum_{l_a l_b j} \mathrm{i}^{l'_a - l'_b - j' + l''_a - l''_b - j'' + l_a - l_b - j} (-1)^{k'_a + k'_b + k''_a + k''_b} (2l_a + 1)(2l_b + 1)(2j + 1)$$
$$\times \begin{pmatrix} l'_a & l''_a & l_a \\ k'_a & k''_a & k_a \end{pmatrix} \begin{pmatrix} l'_b & l''_b & l_b \\ k'_b & k''_b & k_b \end{pmatrix} \begin{pmatrix} j' & j'' & j \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l'_a & l''_a & l_a \\ l'_b & l''_b & l_b \\ j' & j'' & j \end{Bmatrix} S^{k_a k_b}_{l_a l_b j}, \tag{3}$$

where the expression in braces is a Wigner $9j$ symbol [21]. Stone [12] and Price et al. [13] used this expansion formula and shift operators for the molecular angular momenta in the molecule-fixed frames

$$L'_{1\pm} S^{k_a k_b}_{l_a l_b j} = \sqrt{l_a(l_a+1) - k_a(k_a \mp 1)}\, S^{(k_a \mp 1) k_b}_{l_a l_b j}, \tag{4}$$

$$L'_{1\pm} = L'_{1x} \pm \mathrm{i} L'_{1y}, \tag{5}$$

to evaluate explicit formulae for the first S functions and the multipole interaction tensors up to fifth order in $1/R$ in terms of a small set of generating S functions which can be rewritten in terms of simple direction cosines [11–13]. Instead of evaluating explicit formulae for each S function, we shall combine special cases of Eqs. (3) and (4) to give a recurrence relation for the subset of S functions needed for the multipole interaction tensors.

In the following derivation only S functions of even total rank $l_a + l_b + j$ will occur. It is convenient to renormalize these S functions according to:

$$\bar{S}^{k_a k_b}_{l_a l_b j} = \begin{pmatrix} l_a & l_b & j \\ 0 & 0 & 0 \end{pmatrix}^{-1} \times S^{k_a k_b}_{l_a l_b j}. \tag{6}$$

This avoids any factors that contain square roots of rational numbers in the recurrence relations for linear molecules, i.e. for the functions $\bar{S}^{00}_{l_a,l_b,l_a+l_b}$. It should be noted that the renormalization (6) can not be applied to S functions with odd total rank, because the $3j$ symbol in (6) vanishes if the sum $l_a + l_b + j$ is odd. For $k'_a = k'_b = k''_a = k''_b = 0$ the expansion (3) of a product of two even S functions yields a sum of even S functions only. Thus a modified expansion formula for the product of two functions of the form $\bar{S}^{00}_{l_a,l_b,l_a+l_b}$ can be obtained by inserting (6) into Eq. (3):

$$\bar{S}^{00}_{l'_a l'_b j'} \cdot \bar{S}^{00}_{l''_a l''_b j''} = \sum_{l_a l_b j} \mathrm{i}^{l'_a - l'_b - j' + l''_a - l''_b - j'' + l_a - l_b - j} (2l_a+1)(2l_b+1)(2j+1) \bar{S}^{00}_{l_a l_b j}$$
$$\times \begin{pmatrix} l'_a & l'_b & j' \\ 0 & 0 & 0 \end{pmatrix}^{-1} \begin{pmatrix} l''_a & l''_b & j'' \\ 0 & 0 & 0 \end{pmatrix}^{-1} \begin{pmatrix} l_a & l_b & j \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \begin{pmatrix} l'_a & l''_a & l_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_b & l''_b & l_b \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & j'' & j \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l'_a & l''_a & l_a \\ l'_b & l''_b & l_b \\ j' & j'' & j \end{Bmatrix}. \tag{7}$$

The recurrence relation for the functions $\bar{S}^{00}_{l_a,l_b,l_a+l_b}$ are obtained by expanding the products of these functions with the two "generating" functions $\bar{S}^{00}_{011}$ and $\bar{S}^{00}_{110}$. In these cases $l''_a, l''_b, j'' = 0, 1$ and the $3j$ and $9j$ symbols that appear in Eq. (7) can be evaluated using formulae given for example in ref. [21]. One ends up with two relations in which the $\bar{S}$ functions appear with simple rational factors:

$$\bar{S}^{00}_{l_a,l_b,l_a+l_b} \cdot \bar{S}^{00}_{011} = \frac{l_b}{2l_b+1} \bar{S}^{00}_{l_a,l_b-1,l_a+l_b-1} + \frac{l_a+l_b+1}{2l_a+2l_b+1} \bar{S}^{00}_{l_a,l_b+1,l_a+l_b+1}$$
$$- \frac{l_a}{(2l_b+1)(2l_a+2l_b+1)} \bar{S}^{00}_{l_a,l_b+1,l_a+l_b-1}, \tag{8}$$

$$\bar{S}^{00}_{l_a,l_b,l_a+l_b} \cdot \bar{S}^{00}_{110} = \frac{l_a+l_b+1}{(2l_a+1)(2l_b+1)} \bar{S}^{00}_{l_a+1,l_b+1,l_a+l_b}$$
$$+ \frac{l_b}{2l_b+1} \bar{S}^{00}_{l_a+1,l_b-1,l_a+l_b} + \frac{l_a}{2l_a+1} \bar{S}^{00}_{l_a-1,l_b+1,l_a+l_b}. \tag{9}$$

Eq. (8) is solved for $\bar{S}^{00}_{l_a,l_b+1,l_a+l_b+1}$, while Eq. (8) is used to eliminate $\bar{S}^{00}_{l_a,l_b+1,l_a+l_b-1}$ which is the only $\bar{S}$ function in Eq. (8) which is not related to a multipole interaction tensor. Therefore we shift the quantum number l_a in Eq. (8) to $l_a - 1$. Combining both equations yields a recurrence relation for the functions $\bar{S}^{00}_{l_a,l_b,l_a+l_b}$:

$$\bar{S}^{00}_{l_a,l_b+1,l_a+l_b+1} = \frac{1}{l_a+l_b+1} \left(\frac{l_a(l_a-1)}{l_a+l_b} \bar{S}^{00}_{l_a-2,l_b+1,l_a+l_b-1} - \frac{l_b(2l_a+l_b)}{l_a+l_b} \bar{S}^{00}_{l_a,l_b-1,l_a+l_b-1} \right.$$
$$\left. + (2l_a+2l_b+1) \bar{S}^{00}_{l_a,l_b,l_a+l_b} \cdot \bar{S}^{00}_{011} + \frac{l_a(2l_a-1)}{l_a+l_b} \bar{S}^{00}_{l_a-1,l_b,l_a+l_b-1} \cdot \bar{S}^{00}_{110} \right). \tag{10}$$

Introducing the latter equation into Eq. (2) one obtains a recurrence relation for the multipole interaction tensors for linear molecules:

$$T^{(l_a,l_b+1)}_{00} = R^{-2} T^{(l_a-2,l_b+1)}_{00} - \frac{2l_a+l_b}{l_b+1} R^{-2} T^{(l_a,l_b-1)}_{00}$$
$$+ \frac{2l_a+2l_b+1}{l_b+1} R^{-1} \bar{S}^{00}_{011} T^{(l_a,l_b)}_{00} + \frac{2l_a-1}{l_b+1} R^{-2} \bar{S}^{00}_{110} T^{(l_a-1,l_b)}_{00}. \tag{11}$$

In addition to Eq. (11) a second recurrence relation is needed for the multipole-charge interaction tensors $T^{(l_a,0)}_{00}$. It can be obtained from Eq. (11) by setting l_a to zero and exchanging the indices of the molecules:

$$T^{(l_a+1,0)}_{00} = \frac{2l_a+1}{l_a+1} R^{-1} \bar{S}^{00}_{101} T^{(l_a,0)}_{00} - \frac{l_a}{l_a+1} R^{-2} T^{(l_a-1,0)}_{00}. \tag{12}$$

The generalization of these recurrence relations to interactions between non-linear molecules is achieved via the shift relation (4) which can be used to relate the tensors $T^{(l_a,l_b)}_{k_a k_b}$ to the subset $T^{(l_a,l_b)}_{00}$:

$$T^{(l_a,l_b)}_{\pm k_a, \pm k_b} = N(l_a,k_a) N(l_b,k_b) (L'_{a\mp})^{k_a} (L'_{b\mp})^{k_b} T^{(l_a,l_b)}_{00} \qquad \text{for} \quad k_a, k_b \geq 0, \tag{13}$$

Table 1
Definition of the components of the generating $\bar{S}$ functions used in the recurrence relations for $\widetilde{T}$. If $\boldsymbol{e}^a_x$, $\boldsymbol{e}^a_y$, $\boldsymbol{e}^a_z$, and $\boldsymbol{e}^b_x$, $\boldsymbol{e}^b_y$, $\boldsymbol{e}^b_z$ are unit vectors defining the molecule-fixed axis systems for the molecules A and B and $\boldsymbol{e}^{ab}$ is a unit vector in the direction of the intermolecular distance vector from A to B, then $r^a_\alpha = \boldsymbol{e}^a_\alpha \cdot \boldsymbol{e}^{ab}$, $r^b_\alpha = -\boldsymbol{e}^b_\alpha \cdot \boldsymbol{e}^{ab}$ and $c^{ab}_{\alpha\beta} = \boldsymbol{e}^a_\alpha \cdot \boldsymbol{e}^b_\beta$.

$\bar{S}^{00}_{101} = r^a_z$	$\bar{S}^{00}_{011} = r^b_z$	
$\bar{S}^{+10}_{101} = -\sqrt{\frac{1}{2}}(r^a_x + \mathrm{i}r^a_y)$	$\bar{S}^{0+1}_{011} = -\sqrt{\frac{1}{2}}(r^b_x + \mathrm{i}r^b_y)$	
$\bar{S}^{-10}_{101} = +\sqrt{\frac{1}{2}}(r^a_x - \mathrm{i}r^a_y)$	$\bar{S}^{0-1}_{011} = +\sqrt{\frac{1}{2}}(r^b_x - \mathrm{i}r^b_y)$	
$\bar{S}^{00}_{110} = c^{ab}_{zz}$	$\bar{S}^{0+1}_{110} = -\sqrt{\frac{1}{2}}(c^{ab}_{zx} + \mathrm{i}c^{ab}_{zy})$	$\bar{S}^{0-1}_{110} = +\sqrt{\frac{1}{2}}(c^{ab}_{zx} - \mathrm{i}c^{ab}_{zy})$
$\bar{S}^{+10}_{110} = -\sqrt{\frac{1}{2}}(c^{ab}_{xz} + \mathrm{i}c^{ab}_{yz})$	$\bar{S}^{+1+1}_{110} = +\frac{1}{2}(c^{ab}_{xx} - c^{ab}_{yy} + \mathrm{i}c^{ab}_{xy} + \mathrm{i}c^{ab}_{yx})$	$\bar{S}^{+1-1}_{110} = -\frac{1}{2}(c^{ab}_{xx} + c^{ab}_{yy} - \mathrm{i}c^{ab}_{xy} + \mathrm{i}c^{ab}_{yx})$
$\bar{S}^{-10}_{110} = +\sqrt{\frac{1}{2}}(c^{ab}_{xz} - \mathrm{i}c^{ab}_{yz})$	$\bar{S}^{-1+1}_{110} = -\frac{1}{2}(c^{ab}_{xx} + c^{ab}_{yy} + \mathrm{i}c^{ab}_{xy} - \mathrm{i}c^{ab}_{yx})$	$\bar{S}^{-1-1}_{110} = +\frac{1}{2}(c^{ab}_{xx} - c^{ab}_{yy} - \mathrm{i}c^{ab}_{xy} - \mathrm{i}c^{ab}_{yx})$

with the factors $N(l,k)$ defined as

$$N(l,k) = \prod_{m=1}^{|k|}[l(l+1) - m(m-1)]^{-\frac{1}{2}} = \sqrt{\frac{(l+|k|)!}{(l-|k|)!}}. \tag{14}$$

If the shift operators are applied to a product of S functions and interaction tensors, the product rule

$$L'_{a\mp}\left(S^{k_a k_b}_{l_a l_b j} T^{(l'_a,l'_b)}_{k'_a k'_b}\right) = \left(L'_{a\mp} S^{k_a k_b}_{l_a l_b j}\right) T^{(l'_a,l'_b)}_{k'_a k'_b} + S^{k_a k_b}_{l_a l_b j}\left(L'_{a\mp} T^{(l'_a,l'_b)}_{k'_a k'_b}\right) \tag{15}$$

must be obeyed. To simplify the notation we define modified interaction tensors $\widetilde{T}$ as:

$$\widetilde{T}^{(l_a,l_b)}_{\pm k_a,\pm k_b} = R^{l_a+l_b+1}(L'_{a\mp})^{k_a}(L'_{b\mp})^{k_b} T^{(l_a,l_b)}_{00}. \tag{16}$$

For $|k_a| \le l_a$ and $|k_b| \le l_b$ the modified interaction tensors $\widetilde{T}$ are related to the tensors T according to:

$$T^{(l_a,l_b)}_{\pm k_a,\pm k_b} = R^{-l_a-l_b-1} N(l_a,k_a) N(l_b,k_b) \widetilde{T}^{(l_a,l_b)}_{k_a k_b}. \tag{17}$$

For $|k_a| > l_a$ or $|k_b| > l_b$ the components of T and $\widetilde{T}$ vanish. Inserting (11) into Eq. (16) one obtains general recurrence relations for the complex spherical multipole interaction tensors:

$$\begin{aligned}\widetilde{T}^{(l_a,l_b+1)}_{\pm k_a,\pm k_b} = {} & \widetilde{T}^{(l_a-2,l_b+1)}_{\pm k_a,\pm k_b} - \frac{2l_a+l_b}{l_b+1}\widetilde{T}^{(l_a,l_b-1)}_{\pm k_a,\pm k_b} + \frac{2l_a+2l_b+1}{l_b+1}\left(\bar{S}^{00}_{011}\widetilde{T}^{(l_a,l_b)}_{\pm k_a,\pm k_b} + \sqrt{2}\,k_b \bar{S}^{0,\pm1}_{011}\widetilde{T}^{(l_a,l_b)}_{\pm k_a,\pm(k_b-1)}\right) \\ & + \frac{2l_a-1}{l_b+1}\left(\bar{S}^{00}_{110}\widetilde{T}^{(l_a-1,l_b)}_{\pm k_a,\pm k_b} + \sqrt{2}\,k_a \bar{S}^{\pm1,0}_{110}\widetilde{T}^{(l_a-1,l_b)}_{\pm(k_a-1),\pm k_b}\right. \\ & \left. + \sqrt{2}\,k_b \bar{S}^{0,\pm1}_{110}\widetilde{T}^{(l_a-1,l_b)}_{\pm k_a,\pm(k_b-1)} + 2k_a k_b \bar{S}^{\pm1,\pm1}_{110}\widetilde{T}^{(l_a-1,l_b)}_{\pm(k_a-1),\pm(k_b-1)}\right)\end{aligned} \tag{18}$$

The elements of the "generating" $\bar{S}$ functions are defined in Table 1.

3. Recurrence relations for real spherical interaction tensors

For most applications it will be convenient to use real linear combinations of the standard complex spherical components. The real spherical moments $Q_{l\kappa}$ are usually defined in terms of the complex moments $Q^{(l)}_k$ by means of the transformation [11]:

Table 2
Definition of the coefficients $M_{\mu,\kappa}$ and the index function $\eta(\mu,\kappa)$.

μ	κ	$M_{\mu,\kappa}$	$\eta(\mu,\kappa)$	μ	κ	$M_{\mu,\kappa}$	$\eta(\mu,\kappa)$
x	0	$M_{x,0}=0$		y	0	$M_{y,0}=0$	
	$1c$	$M_{x,1c}=\sqrt{2}$	$\eta(x,1c)=0$		$1c$	$M_{y,1c}=0$	$\eta(x,1c)=0$
	$1s$	$M_{x,1s}=0$			$1s$	$M_{y,1s}=\sqrt{2}$	
	$kc, k\geq 2$	$M_{x,kc}=+k$	$\eta(x,kc)=(k-1)c$		$kc, k\geq 2$	$M_{y,kc}=-k$	$\eta(y,kc)=(k-1)s$
	$ks, k\geq 2$	$M_{x,ks}=+k$	$\eta(x,ks)=(k-1)s$		$ks, k\geq 2$	$M_{y,ks}=+k$	$\eta(y,ks)=(k-1)c$
z	κ	$M_{z,\kappa}=1$	$\eta(z,\kappa)=\kappa$				

$$Q_{l,0}=Q_0^{(l)}, \tag{19}$$

$$Q_{l,kc}=\frac{1}{\sqrt{2}}[(-1)^k Q_k^{(l)}+Q_{-k}^{(l)}], \qquad Q_{l,ks}=\frac{1}{\mathrm{i}\sqrt{2}}[(-1)^k Q_k^{(l)}-Q_{-k}^{(l)}], \quad k>0. \tag{20}$$

Formally, this transformation can be written as

$$Q_{l\kappa}=\sum_{m=-l}^{+l} X_{\kappa,m}^{(l)} Q_m^{(l)}, \tag{21}$$

with the unitary transformation matrices $X^{(l)}$ defined by

$$X_{\kappa,m}^{(l)}=\begin{cases} 1 & \text{for } \kappa=0, \quad m=0, \\ (-1)^{|m|}/\sqrt{2} & \text{for } \kappa=|m|c, \ m>0, \\ 1/\sqrt{2} & \text{for } \kappa=|m|c, \ m<0, \\ (-1)^{|m|}/\mathrm{i}\sqrt{2} & \text{for } \kappa=|m|s, \ m>0, \\ -1/\mathrm{i}\sqrt{2} & \text{for } \kappa=|m|s, \ m<0, \\ 0 & \text{else.} \end{cases} \tag{22}$$

The analogous transformation for the multipole interaction tensors is:

$$T_{l_a\kappa_a,l_b\kappa_b}=\sum_{m_a m_b} X_{\kappa_a m_a}^{(l_a)} X_{\kappa_b m_b}^{(l_b)} T_{m_a m_b}^{(l_a l_b)}. \tag{23}$$

Although it would be possible to calculate the complex spherical interaction tensors via equation (18) and transform them afterwards to the real spherical representation, it is computationally more efficient to transform the recurrence relations to the real spherical representation. To obtain a compact notation we introduce the factors $M_{\mu,\kappa}$ and the index function $\eta(\mu,\kappa)$, defined by the relations given in Table 2. Using M and η, the recurrence relations for the real spherical multipole interaction tensors can be written as:

$$\tilde{T}_{(l_a+1)\kappa_a,0}=\frac{2l_a+1}{l_a+1}\sum_{\mu_a} M_{\mu_a,\kappa_a} r_{\mu_a}^a \tilde{T}_{l_a\eta(\mu_a,\eta_a),00}-\frac{l_a}{l_a+1}\tilde{T}_{(l_a-1)\kappa_a,0}, \tag{24}$$

$$\begin{aligned}\tilde{T}_{l_a\kappa_a,(l_b+1)\kappa_b}=&\tilde{T}_{(l_a-2)\kappa_a,(l_b+1)\kappa_b}-\frac{2l_a+l_b}{l_b+1}\tilde{T}_{l_a\kappa_a,(l_b-1)\kappa_b}+\frac{2l_a+2l_b+1}{l_b+1}\sum_{\mu_b} M_{\mu_b,\kappa_b} r_{\mu_b}^b \tilde{T}_{l_a\kappa_a,l_b\eta(\mu_b,\kappa_b)} \\ &+\frac{2l_a-1}{l_b+1}\sum_{\mu_a,\mu_b} M_{\mu_a,\kappa_a} M_{\mu_b,\kappa_b} c_{\mu_a\mu_b}^{ab} \tilde{T}_{(l_a-1)\eta(\mu_a,\kappa_a),l_b\eta(\mu_b,\kappa_b)},\end{aligned} \tag{25}$$

with the sums taken over $\mu_a, \mu_b \in \{x, y, z\}$. The coefficients r^a_μ and r^b_μ are real linear combinations of $S^{k_a 0}_{101}$ and $S^{0 k_b}_{011}$, respectively. They can be interpreted as direction cosines describing the orientation of the intermolecular distance vector in the molecule-fixed coordinate systems of the two molecules. The matrix c^{ab} describes the transformation from the molecule-fixed coordinate system of molecule B to the coordinate system of molecule A. The matrix elements $c^{ab}_{\mu_a \mu_b}$ are real linear combinations of $S^{k_a k_b}_{110}$.

4. Factorization of the spherical interaction tensors and recurrence relations for the rotation matrices for complex and real spherical tensors

By inspection of Eq. (1) one finds that the S-function and Coulomb interaction tensors T become especially simple if the intermolecular distance vector is parallel to the z-axes of the global frame. For this special orientation the $D^{(l)}_{m0}(\Omega_{ab})$ vanish for $m \neq 0$ and Eq. (1) reduces to:

$$S^{k_a k_b}_{l_a l_b j}(\Omega_a, \Omega_b, 0) = \mathrm{i}^{l_a - l_b - j} \sum_m D^{(l_a)}_{m k_a}(\Omega_a)^* D^{(l_b)}_{m k_b}(\Omega_b)^* \begin{pmatrix} l_a & l_b & j \\ m & m & 0 \end{pmatrix}. \tag{26}$$

This simplification can be used to write the matrix of spherical interaction tensors for arbitrary orientations as a product of three sparse matrices by introducing an intermediate transformation to a coordinate system with the z-axes parallel to the intermolecular distance vector:

$$\begin{aligned} T^{(l_a,l_b)}_{k_a,k_b} &= \frac{(-1)^{l_b}}{4\pi\epsilon_0} R^{-l_a-l_b-1} \begin{pmatrix} l_a + l_b \\ l_a \end{pmatrix} \begin{pmatrix} l_a & l_b & l_a + l_b \\ 0 & 0 & 0 \end{pmatrix}^{-1} \\ &\quad \times \sum_{m k'_a k'_b} D^{(l_a)}_{m k'_a}(\Omega^{-1}_{ab})^* D^{(l_a)}_{k'_a k_a}(\Omega_a)^* D^{(l_b)}_{m k'_b}(\Omega^{-1}_{ab})^* D^{(l_b)}_{k'_b k_b}(\Omega_b)^* \begin{pmatrix} l_a & l_b & l_a + l_b \\ m & m & 0 \end{pmatrix} \qquad (27) \\ &= R^{-l_a-l_b-1} \sum_m D^{(l_a)}_{m k_a}(\Omega^{-1}_{ab}\Omega_a)^* D^{(l_b)}_{m k_b}(\Omega^{-1}_{ab}\Omega_b)^* t^{(l_a,l_b)}_m(r_{ab}), \qquad (28) \end{aligned}$$

where $\Omega^{-1}_{ab}\Omega_a$ denotes the result of a rotation by Euler angles Ω_a followed by the inverse of a rotation by angles Ω_{ab},

$$D^{(l_a)}_{m k_a}(\Omega^{-1}_{ab}\Omega_a)^* = \sum_{k'_a} D^{(l_a)}_{m k'_a}(\Omega^{-1}_{ab})^* D^{(l_a)}_{k'_a k_a}(\Omega_a)^*. \tag{29}$$

The numerical coefficients $t^{(l_a,l_b)}_m$ are defined as:

$$\begin{aligned} t^{(l_a,l_b)}_m &= \frac{(-1)^{l_b}}{4\pi\epsilon_0} \begin{pmatrix} l_a + l_b \\ l_a \end{pmatrix} \begin{pmatrix} l_a & l_b & l_a + l_b \\ 0 & 0 & 0 \end{pmatrix}^{-1} \begin{pmatrix} l_a & l_b & l_a + l_b \\ m & m & 0 \end{pmatrix} \\ &= \frac{(-1)^{l_b}}{4\pi\epsilon_0} \sqrt{\begin{pmatrix} l_a + l_b \\ l_a + m \end{pmatrix}} \sqrt{\begin{pmatrix} l_a + l_b \\ l_a - m \end{pmatrix}}. \end{aligned} \tag{30}$$

For each of the three matrices $D^{(l)}_{mk}(\Omega_a \Omega^{-1}_{ab})$, $D^{(l)}_{mk}(\Omega_b \Omega^{-1}_{ab})^*$ and $t^{(l_a,l_b)}_m$ the number of nonvanishing elements up to rank $l_a = l_b = l$ scales only as l^3. Thus, if the Coulomb interaction tensors are not needed explicitly but only a linear transformation of a vector of multipole moments $Q^{(l)}_m$ or a matrix of multipole–multipole polarizabilities $\alpha^{(l,l')}_{mm'}$ with $T^{(l_a,l_b)}_{k_a,k_b}$, it will, for higher ranks, be computationally more efficient to use three successive linear transformations with the Wigner rotation matrices and the matrices $t^{(l_a,l_b)}$.

This is correct with the understanding that all nonvanishing elements of these matrices up to rank $l_a = l_b = l$ can be calculated by algorithms that also scale only as l^3. The coefficients $t_m^{(l_a,l_b)}$ can be obtained from the (precalculated) square roots of $(2l+1)(l+1)$ binomial coefficients. For the Wigner rotation matrices in the complex spherical representation several recurrence relations can be found in the literature [21,22]. We start from the well-known recurrence relation for the Legendre polynomials [21] which are identical to the rotation matrices $D_{00}^{(l)}$:

$$D_{00}^{(l+1)} = \frac{1}{l+1}[(2l+1)D_{00}^{(1)}D_{00}^{(l)} - lD_{00}^{(l-1)}]. \tag{31}$$

The recurrence relations for $m, m' \neq 0$ are again derived using shift relations [21]:

$$L_{\pm}D_{mm'}^{(l)} = \sqrt{l(l+1) - m(m\pm 1)}\,D_{m\pm 1,m'}^{(l)}, \tag{32}$$

$$L'_{\mp}D_{mm'}^{(l)} = \sqrt{l(l+1) - m'(m'\pm 1)}\,D_{m,m'\pm 1}^{(l)}, \tag{33}$$

and, as for the interaction tensors, we introduce modified rotation matrices

$$\tilde{D}_{mm'}^{(l)} = (L_{\pm})^{|m|}(L'_{\mp})^{|m'|}D_{00}^{(l)}, \tag{34}$$

$$D_{mm'}^{(l)} = N(l,m)N(l,m')\tilde{D}_{mm'}^{(l)}. \tag{35}$$

Using Eqs. (31)–(35), the recurrence relations for the complex spherical $\tilde{D}_{m'm}^{(l)}$ are obtained as:

$$\begin{aligned}\tilde{D}_{mm'}^{(l+1)} = \frac{2l+1}{l+1}\{&|m||m'|\tilde{D}_{\pm1,\pm1}^{(1)}\tilde{D}_{m\mp1,m'\mp1}^{(l)} + |m|\tilde{D}_{\pm1,0}^{(1)}\tilde{D}_{m\mp1,m'}^{(l)} \\ &+|m'|\tilde{D}_{0,\pm1}^{(1)}\tilde{D}_{m,m'\mp1}^{(l)} + \tilde{D}_{0,0}^{(1)}\tilde{D}_{m,m'}^{(l)}\} - \frac{l}{l+1}\tilde{D}_{m,m'}^{(l-1)}.\end{aligned} \tag{36}$$

The rotation matrices for the real spherical representation are obtained by transformation of Eq. (36). Employing again $M_{\mu,\kappa}$ and $\eta(\mu,\kappa)$, the recurrence relation for the rotation matrices ${}^rD$ for real spherical tensors can be written as:

$${}^r\tilde{D}_{\kappa_1,\kappa_2}^{(l+1)} = \frac{2l+1}{l+1}\sum_{\mu_1\mu_2} M_{\mu_1,\kappa_1}M_{\mu_2,\kappa_2}R_{\mu_1\mu_2}\,{}^r\tilde{D}_{\eta(\mu_1,\kappa_1)\eta(\mu_2,\kappa_2)}^{(l)} - \frac{l}{l+1}{}^r\tilde{D}_{\kappa_1\kappa_2}^{(l-1)}, \tag{37}$$

$${}^rD_{\kappa_1,\kappa_2}^{(l)} = N(l,|\kappa_1|)N(l,|\kappa_2|)\,{}^r\tilde{D}_{\kappa_1,\kappa_2}^{(l)}, \tag{38}$$

where $R_{\mu_1\mu_2}$ is the 3×3 rotation matrix for a Cartesian vector. Similar recurrence relations for the rotation matrices of real spherical tensors have also been derived by Ivanic and Ruedenberg [23]. The coefficients $t_m^{(l_a,l_b)}$ are easily transformed to the real spherical representation:

$${}^rt_{\kappa}^{(l_a,l_b)} = \begin{cases} t_0^{(l_a,l_b)} & \text{for } \kappa = 0. \\ t_k^{(l_a,l_b)} & \text{for } \kappa = kc \text{ or } \kappa = ks. \end{cases} \tag{39}$$

5. Calculation of multipole expanded interaction energies

In the real spherical tensor formalism the electrostatic interaction is obtained as the bilinear product:

$$E_{es}^{AB}(\mathbf{R},\Omega_a,\Omega_b) = \sum_{\substack{l_a\kappa_a \\ l_b\kappa_b}} Q_{l_a\kappa_a}^{A,mf_a}T_{l_a\kappa_a,l_b\kappa_b}^{AB}(\mathbf{R},\Omega_a,\Omega_b)Q_{l_b\kappa_b}^{B,mf_b}, \tag{40}$$

where Q^{A,mf_a} and Q^{B,mf_b} are the multipole moments of molecules A and B, given in the respective molecule-fixed coordinate systems, denoted by mf_a and mf_b. If the proposed factorization of the interaction tensors

$$T^{AB}_{l_a\kappa_a,l_b\kappa_b}(\mathbf{R},\Omega_a,\Omega_b) = R^{-l_a-l_b-1}\sum_{\kappa} {}^{r}D^{(l_a)}_{\kappa\kappa_a}(\Omega^{-1}_{ab}\Omega_a)\,{}^{r}t^{(l_a,l_b)}_{\kappa}\,{}^{r}D^{(l_b)}_{\kappa\kappa_b}(\Omega^{-1}_{ab}\Omega_b), \tag{41}$$

is inserted into Eq. (40) the electrostatic interaction energy can be evaluated through order L with $O(L^3)$ operations via the expressions:

$$Q^{B,idv}_{l\kappa} = \sum_{\kappa'} {}^{r}D^{l}_{\kappa\kappa'}(\Omega^{-1}_{ab}\Omega_b)\,Q^{B,mf_b}_{l\kappa'}, \tag{42}$$

$$V^{AB,idv}_{l\kappa} = \sum_{l'} R^{-l-l'-1}\,{}^{r}t^{(l,l')}_{\kappa}\,Q^{B,idv}_{l'\kappa}, \tag{43}$$

$$V^{AB,mf_a}_{l,\kappa} = \sum_{\kappa'} {}^{r}D^{l}_{\kappa'\kappa}(\Omega^{-1}_{ab}\Omega_a)\,V^{AB,idv}_{l,\kappa'}, \tag{44}$$

$$E^{AB}_{es} = \sum_{l\kappa} Q^{A,mf_a}_{l\kappa}\,V^{AB,mf_a}_{l\kappa}, \tag{45}$$

where "idv" denotes the intermediate coordinate system with the z-axes parallel to the intermolecular distance vector $\mathbf{R}$ and $V^{AB,idv}$ and V^{AB,mf_a} are the expansion coefficients of the electrostatic potential at the origin of molecule A due to the multipole moments of molecule B in the intermediate coordinate system "idv" and in the molecule-fixed system mf_a.

If the second-order induction energy of an assembly of molecules is calculated via electrostatic potential coefficients and induced multipole moments as intermediates,

$$V^{B,mf_b}_{l\kappa} = \sum_{A\neq B} V^{BA,mf_b}_{l\kappa}, \tag{46}$$

$${}^{ind}Q^{B,mf_b}_{l\kappa} = -\sum_{l'\kappa'} \alpha^{B,mf_b/mf_b}_{l\kappa,l'\kappa'}\,V^{B,mf_b}_{l'\kappa'}, \tag{47}$$

$$E_{ind} = \tfrac{1}{2}\sum_{B}\sum_{l\kappa} {}^{ind}Q^{B,mf_b}_{l\kappa}\,V^{B,mf_b}_{l\kappa}, \tag{48}$$

the rate-determining steps, the calculation of V^{B,mf_b} via Eqs. (42)–(44) and (46) and the calculation of ${}^{ind}Q^{B,mf_b}$ via Eq. (47), require $O(N^2_{mol}) \times O(L^3)$ and $O(N_{mol}) \times O(L^4)$ operations, where N_{mol} is the number of molecules in the assembly.

The second-order dispersion interaction between two molecules A and B is obtained within the real spherical tensor formalism from the frequency-dependent multipole–multipole polarizabilities in the molecule-fixed coordinate systems as:

$$E^{AB}_{disp} = -\frac{1}{2\pi}\int_0^{\infty} d\omega \sum_{\substack{l_a\kappa_a\\ l_b\kappa_b}}\sum_{\substack{l'_a\kappa'_a\\ l'_b\kappa'_b}} \alpha^{A,mf_a/mf_a}_{l_a\kappa_a l'_a\kappa'_a}(i\omega)\,T^{AB}_{l_a\kappa_a l_b\kappa_b}(\mathbf{R},\Omega_a,\Omega_b)\,T^{AB}_{l'_a\kappa'_a l'_b\kappa'_b}(\mathbf{R},\Omega_a,\Omega_b)\,\alpha^{B,mf_b/mf_b}_{l_b\kappa_b l'_b\kappa'_b}(i\omega). \tag{49}$$

Usually the dispersion energy is calculated via so-called Casimir–Polder or dispersion integrals as intermediates [11,24]:

$$X^{AB}_{l_a\kappa_a l'_a\kappa'_a l_b\kappa_b l'_b\kappa'_b} = -\frac{1}{2\pi}\int_0^{\infty} d\omega\, \alpha^{A,mf_a/mf_a}_{l_a\kappa_a l'_a\kappa'_a}(i\omega)\,\alpha^{B,mf_b/mf_b}_{l_b\kappa_b l'_b\kappa'_b}(i\omega) \tag{50}$$

$$E_{\mathrm{disp}}^{\mathrm{AB}} = \sum_{\substack{l_a\kappa_a \\ l_b\kappa_b}} \sum_{\substack{l'_a\kappa'_a \\ l'_b\kappa'_b}} T^{\mathrm{AB}}_{l_a\kappa_a l_b\kappa_b} T^{\mathrm{AB}}_{l'_a\kappa'_a l'_b\kappa'_b} X^{\mathrm{AB}}_{l_a\kappa_a l'_a\kappa'_a l_b\kappa_b l'_b\kappa'_b}. \tag{51}$$

The direct use of Eqs. (50) and (51) would require the determination and storage of $(L+1)^8$ coefficients X^{AB}. Therefore in most applications the coefficients X^{AB} are transformed to a coupled representation with polarizabilities $\alpha^{L,M}_{l,l'}$ and dispersion coefficients $C_n^{L_a,M_a,L_b,M_b,L}$ which are irreducible tensors of $SO(3)$ [20,25]. Thereby the number of coefficients and interaction tensors reduces to $\mathrm{O}(L^6)$ components, because in the irreducible representation the interaction functions depend only on the coupled angular momenta L_a and L_b but not on the individual components l_a, l'_a, l_b and l'_b. For atoms and for highly symmetric molecules there are also far fewer non-zero irreducible polarizabilities and dispersion coefficients than there are dispersion integrals in the uncoupled representation. In particular, the irreducible representation is convenient for atom-atom and atom-diatom Van der Waals complexes due to the small fraction of non-vanishing irreducible dispersion coefficients.

For dimers built from large non-spherical molecules, however, a one-centre multipole expansion of the second-order dispersion energy in terms of frequency-dependent molecular polarizabilities is not suitable for an accurate describtion of Van der Waals interactions and a distributed multipole expansion of the dispersion interaction, as proposed e.g. in Ref. [11], should be employed [26]. For a distributed multipole expansion the irreducible representation does not provide a useful scheme for computing interaction energies, because the two index pairs l,κ and l',κ' are for distributed polarizabilities in general related to different expansion centers and the coulomb interaction tensors in Eq. (51) also depend on different distance vectors. Thus, with a distributed multipole expansion an uncoupled formulation must be used.

The operation count and storage requirements for the computation of dispersion energies within the uncoupled formulation can be reduced considerably by employing the proposed factorization of the interaction tensors, if the integration over the frequencies ω is carried out by means of a numerical quadrature with N_{grid} grid points ω_j and weights $W(\omega_j)$. In this case Eq. (49) can be factorized into several steps using Eq. (41),

$$\alpha^{\mathrm{A},mf_a/\mathrm{idv}}_{l_1\kappa_1,l_2\kappa_2}(\omega_j) = \sum_{\kappa'} {}^{r}D^{l_2}_{\kappa_2\kappa'}(\Omega_{ab}^{-1}\Omega_a)\,\alpha^{\mathrm{A},mf_a/mf_a}_{l_1\kappa_1,l_2\kappa'}(\omega_j), \tag{52}$$

$$S^{\mathrm{AB},mf_a/\mathrm{idv}}_{l_a\kappa_a l_b\kappa_b}(\omega_j) = \sum_{l'} \alpha^{\mathrm{A},mf_a/\mathrm{idv}}_{l_a\kappa_a,l'\kappa_b}(\omega_j)\,{}^{r}t^{(l',l_b)}_{\kappa_b} R^{-l'-l_b-1}, \tag{53}$$

$$S^{\mathrm{AB},mf_a/mf_b}_{l_a\kappa_a l_b\kappa_b}(\omega_j) = \sum_{\kappa'} {}^{r}D^{(l_b)}_{\kappa'\kappa_b}(\Omega_{ab}^{-1}\Omega_b)\,S^{\mathrm{AB},mf_a/\mathrm{idv}}_{l_a\kappa_a l_b\kappa'}(\omega_j), \tag{54}$$

$$E_{\mathrm{disp}}^{\mathrm{AB}} = -\sum_j \frac{1}{2\pi} W(\omega_j) \sum_{\substack{l_a\kappa_a \\ l_b\kappa_b}} S^{\mathrm{AB},mf_a/mf_b}_{l_a\kappa_a l_b\kappa_b}(\omega_j)\,S^{\mathrm{BA},mf_b/mf_a}_{l_b\kappa_b l_a\kappa_a}(\omega_j), \tag{55}$$

of which the most expensive (52)–(54) require $N_{\mathrm{grid}}\times\mathrm{O}(L^5)$ cpu time and storage of $2\times(L+1)^4$ intermediates S^{AB} and S^{BA}. If for example a Gauss–Chebyshev scheme is used as described in Ref. [27], between 5 and 7 grid points will usually be sufficient to converge $E_{\mathrm{disp}}^{\mathrm{AB}}$ better than 0.1%.

One advantage of the factorization (41) which we have not employed until now, is that it separates the dependence of the interaction tensors on the relative orientations of molecules A and B and the vector $\mathbf{R}$ into three independent functions: ${}^{r}D^{(l_a)}_{\kappa\kappa_a}(\Omega_{ab}^{-1}\Omega_a)$, which depends only on the relative orientation of molecule A and the intermolecular distance vector, ${}^{r}D^{(l_b)}_{\kappa\kappa_b}(\Omega_{ab}^{-1}\Omega_b)$, the counterpart for molecule B, and $R^{-l_a-l_b-1}$. This separation will significantly simplify the calculation of derivatives for the interaction energies, i.e. forces and torques, because now only derivatives for the less complex functions ${}^{r}D$ and ${}^{r}t$ need be calculated and many intermediates can be shared with the calculation of the energies. Work on this subject is in progress.

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