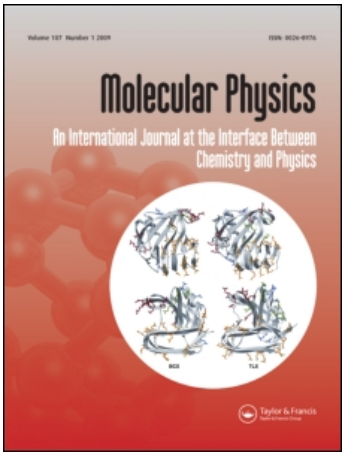
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Calculation of orientation-dependent double-tensor moments for Coulomb-type intermolecular interactions

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A new derivation is presented for the orientation-dependent interaction tensors which describe the electrostatic interaction between two multipole or multipole polarizability distributions both given in their own molecule-fixed coordinate system. This derivation leads to an explicit equations that allows easy and direct evaluation of formulae for the components of the double-tensors and also for high ranks. Such an equation is given for the real, complex spherical, and cartesian moments. The formula is suitable for providing stable computer-generated expressions for tensor operators of any rank.

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1. Introduction

Long-range intermolecular interactions, e.g. first-order electrostatic energy, induction energy and dispersion energy, are often approximated by a multipole expansion up to an appropriate rank. Then, as frequently pointed out in the literature, all these Coulomb-type interactions can be described with a common set of interaction tensors.

Such a truncated expansion in multipole moments neglects contributions of higher rank tensors and effects arising from interpenetration of molecular charge distributions, but it has the decisive advantage that the monomer charge distributions and their polarization are described with a few parameters. This is especially of importance for calculations of weak interactions between large molecules, for which the Coulomb-type interaction energies, particularly the dispersion energy, cannot be calculated easily within a supermolecular approach.

On expansion of the interaction potentials between two strongly anisotropic molecular charge distributions one has to calculate contributions of moments up to a relatively high rank, at least up to the quadrupoles, in order to achieve acceptable accuracy. We thus face the problem of taking into account the orientational dependence of these contributions, which may involve as many as five independent coordinates. The conventional way to solve this problem is to employ Cartesian tensors. Then the multipole moments or multipole polarizabilities can be transformed into a global coordinate system using the rotation matrices. An analogous approach for real spherical tensor moments has been developed by Magnasco *et al.* [1], but this led to rather complicated transformation matrices for the real spherical tensors comparable with the Wigner rotation matrices for complex spherical tensors.

A more elegant way consists of the use of molecule-fixed moments and the incorporation of the transformation coefficients into orientation-dependent interaction tensors as they were developed for spherical tensors by Tough [2], Price

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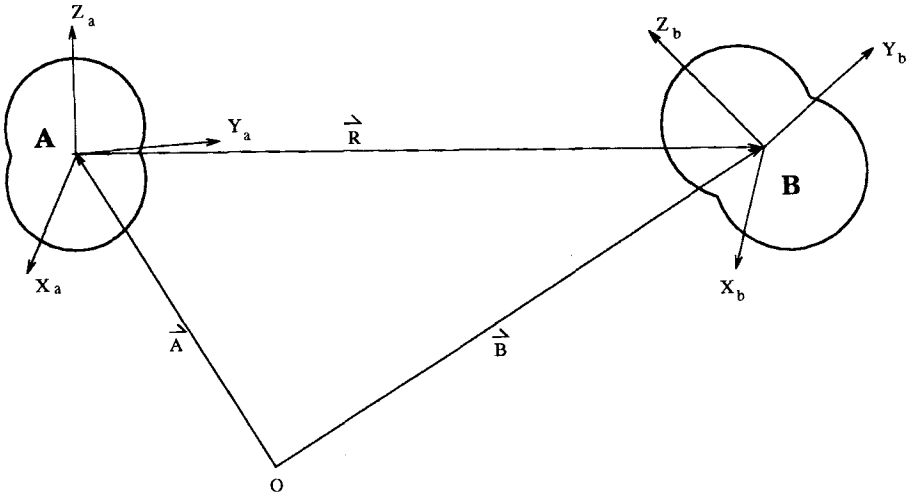


Figure 1. The molecule fixed systems in the global frame.

et al. [3], Stone [4], and Piecuch [5]. This offers the possibility of taking advantage of molecular symmetries, which are reflected by selection rules for the components of tensorial moments in the molecular system of principal axes.

Unfortunately, with the equation given by Price and Stone, the calculation of formulae for the components of the orientation-dependent interaction tensors is very cumbersome, even if one calculates the S functions, which appear in their equation, by the recursive algorithm proposed by Stone [6]. For that reason we present an alternative derivation for the interaction double-tensors which leads to an explicit equation that allows easy and direct calculation of components, even for the higher rank double-tensors.

2. Expansion of the electrostatic interaction energy

The starting point for the derivation is the well-known equation for the interaction energy

$$U_{\mathrm{es}} = \int \frac{\rho^{\mathrm{A}}_{\mathrm{SF}}(\boldsymbol{r}) \cdot \rho^{\mathrm{B}}_{\mathrm{SF}}(\boldsymbol{r}')}{4\pi\epsilon_0 |\boldsymbol{r}' - \boldsymbol{r}|} \, \mathrm{d}^3 r \, \mathrm{d}^3 r' \tag{1}$$

between two charge distributions $\rho^{\mathrm{A}}_{\mathrm{SF}}$ and $\rho^{\mathrm{B}}_{\mathrm{SF}}$, both referred to a space-fixed frame. Writing $\boldsymbol{A}$ and $\boldsymbol{B}$ for the origins and $\Omega_{\mathrm{A}} = (\phi_{\mathrm{a}}, \theta_{\mathrm{a}}, \psi_{\mathrm{a}})$ and $\Omega_{\mathrm{B}} = (\phi_{\mathrm{b}}, \theta_{\mathrm{b}}, \psi_{\mathrm{b}})$ for the Euler angles of the molecule-fixed systems, the transformation from the coordinates $\boldsymbol{r}$ and $\boldsymbol{r}'$ in the global frame to the coordinates $\boldsymbol{r}_{\mathrm{a}}$ and $\boldsymbol{r}_{\mathrm{b}}$ in the molecule-fixed systems is given by (see figure 1)

$$\boldsymbol{r} = \boldsymbol{A} + \hat{R}_{\mathrm{a}} \boldsymbol{r}_{\mathrm{a}} \quad \text{and} \quad \boldsymbol{r}' = \boldsymbol{B} + \hat{R}_{\mathrm{b}} \boldsymbol{r}_{\mathrm{b}}, \tag{2}$$

with

$$\hat{R}_{\mathrm{a}} = \hat{R}(\Omega_{\mathrm{a}}) \quad \text{and} \quad \hat{R}_{\mathrm{b}} = \hat{R}(\Omega_{\mathrm{b}}). \tag{3}$$

Then the relation between the charge distributions $\rho^{\mathrm{A}}_{\mathrm{SF}}$ and $\rho^{\mathrm{B}}_{\mathrm{SF}}$ in the global frame

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Table 1. Electrostatic double-tensor moments up to rank 5.

t	u	$4\pi\epsilon_0 T^{ab}_{tu}$
00	00	$R^{-1}\cdot 1$
1α	00	$R^{-2}\cdot r^a_\alpha$
20	00	$R^{-3}\cdot\frac{1}{2}(3r^{a2}_z-1)$
$21c$	00	$R^{-3}\cdot\sqrt{3}r^a_x r^a_z$
$21s$	00	$R^{-3}\cdot\sqrt{3}r^a_y r^a_z$
$22c$	00	$R^{-3}\cdot\frac{1}{2}\sqrt{3}(r^{a2}_x-r^{a2}_y)$
$22s$	00	$R^{-3}\cdot\sqrt{3}r^a_x r^a_y$
1α	1β	$R^{-3}\cdot(3r^a_\alpha r^b_\beta+c_{\alpha\beta})$
30	00	$R^{-4}\cdot\frac{1}{2}(5r^{a3}_z-3r^a_z)$
$31c$	00	$R^{-4}\cdot\frac{1}{4}\sqrt{6}r^a_x(5r^{a2}_z-1)$
$31s$	00	$R^{-4}\cdot\frac{1}{4}\sqrt{6}r^a_y(5r^{a2}_z-1)$
$32c$	00	$R^{-4}\cdot\frac{1}{2}\sqrt{15}r^a_z(r^{a2}_x-r^{a2}_y)$
$32s$	00	$R^{-4}\cdot\sqrt{15}r^a_x r^a_y r^a_z$
$33c$	00	$R^{-4}\cdot\frac{1}{4}\sqrt{10}(r^{a3}_x-3r^a_x r^{a2}_y)$
$33s$	00	$R^{-4}\cdot\frac{1}{4}\sqrt{10}(3r^{a2}_x r^a_y-r^{a3}_y)$
20	1β	$R^{-4}\cdot\frac{3}{2}(5r^{a2}_z r^b_\beta-r^b_\beta+2r^a_z c_{z\beta})$
$21c$	1β	$R^{-4}\cdot\sqrt{3}(5r^a_x r^a_z r^b_\beta+r^a_x c_{z\beta}+r^a_z c_{x\beta})$
$21s$	1β	$R^{-4}\cdot\sqrt{3}(5r^a_y r^a_z r^b_\beta+r^a_y c_{z\beta}+r^a_z c_{y\beta})$
$22c$	1β	$R^{-4}\cdot\frac{1}{2}\sqrt{3}(5(r^{a2}_x-r^{a2}_y)r^b_\beta+2r^a_x c_{x\beta}-2r^a_y c_{y\beta})$
$22s$	1β	$R^{-4}\cdot\sqrt{3}(5r^a_x r^a_y r^b_\beta+r^a_x c_{y\beta}+r^a_y c_{x\beta})$
40	00	$R^{-5}\cdot\frac{1}{8}(35r^{a4}_z-30r^{a2}_z+3)$
$41c$	00	$R^{-5}\cdot\frac{1}{4}\sqrt{10}r^a_x(7r^{a3}_z-3r^a_z)$
$41s$	00	$R^{-5}\cdot\frac{1}{4}\sqrt{10}r^a_y(7r^{a3}_z-3r^a_z)$

and the charge distributions in the molecule-fixed systems is

$$\rho^{\mathrm{A}}_{\mathrm{SF}}(\boldsymbol{r})=\rho^{\mathrm{A}}_{\mathrm{m}}(\boldsymbol{r}_{\mathrm{a}})\quad\text{and}\quad\rho^{\mathrm{B}}_{\mathrm{SF}}(\boldsymbol{r}')=\rho^{\mathrm{B}}_{\mathrm{m}}(\boldsymbol{r}_{\mathrm{b}}). \tag{4}$$

The intermolecular distance vector is given by

$$\boldsymbol{R}=\boldsymbol{B}-\boldsymbol{A}. \tag{5}$$

Because rotations do not change the length of vectors we obtain

$$\begin{aligned}|\boldsymbol{r}'-\boldsymbol{r}|&=|\boldsymbol{R}+\hat{R}_{\mathrm{b}}\boldsymbol{r}_{\mathrm{b}}-\hat{R}_{\mathrm{a}}\boldsymbol{r}_{\mathrm{a}}|\\&=|\hat{R}^{-1}_{\mathrm{a}}\boldsymbol{R}+\hat{R}^{-1}_{\mathrm{a}}\hat{R}_{\mathrm{b}}\boldsymbol{r}_{\mathrm{b}}-\boldsymbol{r}_{\mathrm{a}}|.\end{aligned}$$

Using these relations in the equation for the electrostatic energy (1) and expanding the potential of $\rho^{\mathrm{A}}_{\mathrm{m}}$ in real spherical multipole moments by neglecting the overlap of

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Table 1. *Continued.*

t	u	$4\pi\epsilon_0 T^{ab}_{tu}$
$42c$	00	$R^{-5}\cdot\frac{1}{4}\sqrt{5}(r_x^{a2}-r_y^{a2})(7r_z^{a2}-1)$
$42s$	00	$R^{-5}\cdot\frac{1}{2}\sqrt{5}r_x^a r_y^a(7r_z^{a2}-1)$
$43c$	00	$R^{-5}\cdot\frac{1}{4}\sqrt{70}r_x^a r_z^a(r_x^{a2}-3r_y^{a2})$
$43s$	00	$R^{-5}\cdot\frac{1}{4}\sqrt{70}r_y^a r_z^a(3r_x^{a2}-r_y^{a2})$
$44c$	00	$R^{-5}\cdot\frac{1}{8}\sqrt{35}(r_x^{a4}-6r_x^{a2}r_y^{a2}+r_y^{a4})$
$44s$	00	$R^{-5}\cdot\frac{1}{2}\sqrt{35}(r_x^{a3}r_y^a-r_x^a r_y^{a3})$
30	1β	$R^{-5}\cdot\frac{1}{2}(5(7r_z^{a3}-3r_z^a)r_\beta^b+3(5r_z^{a2}-1)c_{z\beta})$
$31c$	1β	$R^{-5}\cdot\frac{1}{4}\sqrt{6}(35r_x^a r_z^{a2}r_\beta^b-5r_x^a r_\beta^b+10r_x^a r_z^a c_{z\beta}+5r_z^{a2}c_{x\beta}-c_{x\beta})$
$31s$	1β	$R^{-5}\cdot\frac{1}{4}\sqrt{6}(35r_y^a r_z^{a2}r_\beta^b-5r_y^a r_\beta^b+10r_y^a r_z^a c_{z\beta}+5r_z^{a2}c_{y\beta}-c_{y\beta})$
$32c$	1β	$R^{-5}\cdot\frac{1}{2}\sqrt{15}((r_x^{a2}-r_y^{a2})(7r_z^a r_\beta^b+c_{z\beta})+2r_z^a(r_x^a c_{x\beta}-r_y^a c_{y\beta}))$
$32s$	1β	$R^{-5}\cdot\sqrt{15}(7r_x^a r_y^a r_z^a r_\beta^b+r_x^a r_y^a c_{z\beta}+r_x^a r_z^a c_{y\beta}+r_y^a r_z^a c_{x\beta})$
$33c$	1β	$R^{-5}\cdot\frac{1}{4}\sqrt{10}(7r_x^a(r_x^{a2}-3r_y^{a2})r_\beta^b+3(r_x^{a2}-r_y^{a2})c_{x\beta}-6r_x^a r_y^a c_{y\beta})$
$33s$	1β	$R^{-5}\cdot\frac{1}{4}\sqrt{10}(7r_y^a(3r_x^{a2}-r_y^{a2})r_\beta^b+3(r_x^{a2}-r_y^{a2})c_{y\beta}+6r_x^a r_y^a c_{x\beta})$
20	20	$R^{-5}\cdot\frac{3}{4}(35r_z^{a2}r_z^{b2}-5r_z^{a2}-5r_z^{b2}+20r_z^a r_z^b c_{zz}+2c_{zz}^2+1)$
20	$21c$	$R^{-5}\cdot\frac{1}{2}\sqrt{3}(5r_x^b r_z^b(7r_z^{a2}-1)+10r_z^a(r_x^b c_{zz}+r_z^b c_{zx})+2c_{zx}c_{zz})$
20	$21s$	$R^{-5}\cdot\frac{1}{2}\sqrt{3}(5r_y^b r_z^b(7r_z^{a2}-1)+10r_z^a(r_y^b c_{zz}+r_z^b c_{zy})+2c_{zy}c_{zz})$
20	$22c$	$R^{-5}\cdot\frac{1}{4}\sqrt{3}(5(7r_z^{a2}-1)(r_x^{b2}-r_y^{b2})+20r_z^a(r_x^b c_{zx}-r_y^b c_{zy})+2(c_{zx}^2-c_{zy}^2))$
20	$22s$	$R^{-5}\cdot\frac{1}{2}\sqrt{3}(5(7r_z^{a2}-1)r_x^b r_y^b+10r_z^a(r_x^b c_{zy}+r_y^b c_{zx})+2c_{zx}c_{zy})$
$21c$	$21c$	$R^{-5}\cdot(35r_x^a r_z^a r_x^b r_z^b+5r_x^a r_x^b c_{zz}+5r_x^a r_z^b c_{zx}$ $+5r_z^a r_x^b c_{xz}+5r_z^a r_z^b c_{xx}+c_{xx}c_{zz}+c_{xz}c_{zx})$
$21c$	$21s$	$R^{-5}\cdot(35r_x^a r_z^a r_y^b r_z^b+5r_x^a r_y^b c_{zz}+5r_x^a r_z^b c_{zy}$ $+5r_z^a r_y^b c_{xz}+5r_z^a r_z^b c_{xy}+c_{xy}c_{zz}+c_{xz}c_{zy})$

the charge distributions, we obtain

$$U_{es}=\int\frac{\rho_m^A(\boldsymbol{r}_a)\cdot\rho_m^B(\boldsymbol{r}_b)}{4\pi\epsilon_0|\hat{R}_a^{-1}\boldsymbol{R}+\hat{R}_a^{-1}\hat{R}_b\boldsymbol{r}_b-\boldsymbol{r}_a|}\,d^3r_a\,d^3r_b \tag{6}$$

$$=\frac{1}{4\pi\epsilon_0}\sum_{l_1=0}^{\infty}\sum_{\kappa_1}\int Q^A_{l_1\kappa_1}\cdot I_{l_1\kappa_1}(\hat{R}_a^{-1}R+\hat{R}_a^{-1}\hat{R}_b\boldsymbol{r}_b)\cdot\rho_m^B(\boldsymbol{r}_b)\,d^3r_b, \tag{7}$$

where the index κ_1 runs over the labels $l_1c,\ldots,1c,0,1s,\ldots l_1s$, and the real spherical multipole moments $Q_{l\kappa}$ and the real linear combinations of the irregular spherical harmonics are defined by

$$Q_{l\kappa}=\int\rho(\boldsymbol{r})\cdot R_{l\kappa}(\boldsymbol{r})\,d^3r \tag{8}$$

$$I_{l\kappa}(\boldsymbol{r})=r^{-(l+1)}\cdot C_{l\kappa}(\theta,\varphi), \tag{9}$$

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Table 1. *Continued.*

t	u	$4\pi\epsilon_0 T^{ab}_{tu}$
21c	22c	$R^{-5}\cdot\frac{1}{2}(35r^a_x r^a_z(r^{b2}_x - r^{b2}_y) + 10r^a_x(r^b_x c_{zx} - r^b_y c_{zy})$
		$+10r^a_z(r^b_x c_{xx} - r^b_y c_{xy}) + 2c_{xx}c_{zx} - 2c_{xy}c_{zy})$
21c	22s	$R^{-5}\cdot(35r^a_x r^a_z r^b_x r^b_y + 5r^a_x r^b_x c_{zy} + 5r^a_x r^b_y c_{zx}$
		$+5r^a_z r^b_x c_{xy} + 5r^a_z r^b_y c_{xx} + c_{xx}c_{zy} + c_{xy}c_{zx})$
21s	21s	$R^{-5}\cdot(35r^a_y r^a_z r^b_y r^b_z + 5r^a_y r^b_y c_{zz} + 5r^a_y r^b_z c_{zy}$
		$+5r^a_z r^b_y c_{yz} + 5r^a_z r^b_z c_{yy} + c_{yy}c_{zz} + c_{yz}c_{zy})$
21s	22c	$R^{-5}\cdot\frac{1}{2}(35r^a_y r^a_z(r^{b2}_x - r^{b2}_y) + 10r^a_y(r^b_x c_{zx} - r^b_y c_{zy})$
		$+10r^a_z(r^b_x c_{yx} - r^b_y c_{yy}) + 2c_{yx}c_{zx} - 2c_{yy}c_{zy})$
21s	22s	$R^{-5}\cdot(35r^a_y r^a_z r^b_x r^b_y + 5r^a_y r^b_x c_{zy} + 5r^a_y r^b_y c_{zx}$
		$+5r^a_z r^b_x c_{yy} + 5r^a_z r^b_y c_{yx} + c_{yx}c_{zy} + c_{yy}c_{zx})$
22c	22c	$R^{-5}\cdot\frac{1}{4}(35(r^{a2}_x - r^{a2}_y)(r^{b2}_x - r^{b2}_y) + 20r^a_x r^b_x c_{xx} - 20r^a_x r^b_y c_{xy}$
		$-20r^a_y r^b_x c_{yx} + 20r^a_y r^b_y c_{yy} + 2c^2_{xx} - 2c^2_{xy} - 2c^2_{yx} + 2c^2_{yy})$
22c	22s	$R^{-5}\cdot\frac{1}{2}(35(r^{a2}_x - r^{a2}_y)r^b_x r^b_y + 10r^a_x r^b_x c_{xy} + 10r^a_x r^b_y c_{xx}$
		$-10r^a_y r^b_x c_{yy} - 10r^a_y r^b_y c_{yx} + 2c_{xx}c_{xy} - 2c_{yx}c_{yy})$
22s	22s	$R^{-5}\cdot(35r^a_x r^a_y r^b_x r^b_y + 5r^a_x r^b_x c_{yy} + 5r^a_x r^b_y c_{yx}$
		$+5r^a_y r^b_x c_{xy} + 5r^a_y r^b_y c_{xx} + c_{xx}c_{yy} + c_{xy}c_{yx})$
50	00	$R^{-6}\cdot\frac{1}{8}(63r^{a5}_z - 70r^{a3}_z + 15r^a_z)$
51c	00	$R^{-6}\cdot\frac{1}{8}\sqrt{15}(21r^a_x r^{a4}_z - 14r^a_x r^{a2}_z + r^a_x)$
51s	00	$R^{-6}\cdot\frac{1}{8}\sqrt{15}(21r^a_y r^{a4}_z - 14r^a_y r^{a2}_z + r^a_y)$
52c	00	$R^{-6}\cdot\frac{1}{4}\sqrt{105}(3r^{a3}_z - r^a_z)(r^{a2}_x - r^{a2}_y)$
52s	00	$R^{-6}\cdot\frac{1}{2}\sqrt{105}r^a_x r^a_y(3r^{a3}_z - r^a_z)$
53c	00	$R^{-6}\cdot\frac{1}{16}\sqrt{70}r^a_x(r^{a2}_x - 3r^{a2}_y)(9r^{a2}_z - 1)$
53s	00	$R^{-6}\cdot\frac{1}{16}\sqrt{70}r^a_y(3r^{a2}_x - r^{a2}_y)(9r^{a2}_z - 1)$

with

$$R_{l\kappa}(\boldsymbol{r}) = r^l \cdot C_{l\kappa}(\theta, \varphi) \tag{10}$$

and

$$C_{lkc} = \sqrt{\tfrac{1}{2}}[(-1)^k C^{(l)}_k + C^{(l)}_{-k}] \quad \text{with } k > 0 \tag{11}$$

$$C_{lks} = -i\sqrt{\tfrac{1}{2}}[(-1)^k C^{(l)}_k - C^{(l)}_{-k}], \tag{12}$$

where $C^{(l)}_k$ are Racah normalized spherical harmonics [7].

The next step is the expansion of the functions $I_{l_1\kappa_1}$ with respect to the centre of

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Table 1. *Continued*

t	u	$4\pi\epsilon_0 T^{ab}_{tu}$
54c	00	$R^{-6}\cdot\frac{3}{8}\sqrt{35}(r_x^{a4}r_z^a - 6r_x^{a2}r_y^{a2}r_z^a + r_y^{a4}r_z^a)$
54s	00	$R^{-6}\cdot\frac{3}{2}\sqrt{35}(r_x^{a3}r_y^a r_z^a - r_x^a r_y^{a3}r_z^a)$
55c	00	$R^{-6}\cdot\frac{3}{16}\sqrt{14}(r_x^{a5} - 10r_x^{a3}r_y^{a2} + 5r_x^a r_y^{a4})$
55s	00	$R^{-6}\cdot\frac{3}{16}\sqrt{14}(5r_x^{a4}r_y^a - 10r_x^{a2}r_y^{a3} + r_y^{a5})$
40	1β	$R^{-6}\cdot\frac{5}{8}(63r_z^{a4}r_\beta^b - 42r_z^{a2}r_\beta^b + 28r_z^{a3}c_{z\beta} + 3r_\beta^b - 12r_z^a c_{z\beta})$
41c	1β	$R^{-6}\cdot\frac{1}{4}\sqrt{10}(21(3r_z^{a2}-1)r_x^a r_z^a r_\beta^b + 3(7r_z^{a2}-1)r_x^a c_{z\beta} + (7r_z^{a2}-3)r_z^a c_{x\beta})$
41s	1β	$R^{-6}\cdot\frac{1}{4}\sqrt{10}(21(3r_z^{a2}-1)r_y^a r_z^a r_\beta^b + 3(7r_z^{a2}-1)r_y^a c_{z\beta} + (7r_z^{a2}-3)r_z^a c_{y\beta})$
42c	1β	$R^{-6}\cdot\frac{1}{4}\sqrt{5}(63r_z^{a2}-7)(r_x^{a2}-r_y^{a2})r_\beta^b$
		$+14(r_x^{a2}-r_y^{a2})r_z^a c_{z\beta} + 2(7r_z^{a2}-1)(r_x^a c_{x\beta} - r_y^a c_{y\beta}))$
42s	1β	$R^{-6}\cdot\frac{1}{2}\sqrt{5}((63r_z^{a2}r_\beta^b - 7r_\beta^b + 14r_z^a c_{z\beta})r_x^a r_y^a + (7r_z^{a2}-1)(r_x^a c_{y\beta} + r_y^a c_{x\beta}))$
43c	1β	$R^{-6}\cdot\frac{1}{4}\sqrt{70}(9r_x^{a3}r_z^a r_\beta^b - 27r_x^a r_y^{a2}r_z^a r_\beta^b + r_x^{a3}c_{z\beta}$
		$+3r_x^{a2}r_z^a c_{x\beta} - 3r_x^a r_y^{a2}c_{z\beta} - 6r_x^a r_y^a r_z^a c_{y\beta} - 3r_y^{a2}r_z^a c_{x\beta})$
43s	1β	$R^{-6}\cdot\frac{1}{4}\sqrt{70}(27r_x^{a2}r_y^a r_z^a r_\beta^b - 9r_y^{a3}r_z^a r_\beta^b + 3r_x^{a2}r_y^a c_{z\beta}$
		$+3r_x^{a2}r_z^a c_{y\beta} + 6r_x^a r_y^a r_z^a c_{x\beta} - r_y^{a3}c_{z\beta} - 3r_y^{a2}r_z^a c_{y\beta})$
44c	1β	$R^{-6}\cdot\frac{1}{8}\sqrt{35}(9r_x^{a4}r_\beta^b - 54r_x^{a2}r_y^{a2}r_\beta^b + 9r_y^{a4}r_\beta^b$
		$+4r_x^{a3}c_{x\beta} - 12r_x^{a2}r_y^a c_{y\beta} - 12r_x^a r_y^{a2}c_{x\beta} + 4r_y^{a3}c_{y\beta})$
44s	1β	$R^{-6}\cdot\frac{1}{2}\sqrt{35}(9r_x^a r_y^a(r_x^{a2}-r_y^{a2})r_\beta^b + r_x^a(r_x^{a2}-3r_y^{a2})c_{y\beta} + r_y^a(3r_x^{a2}-r_y^{a2})c_{x\beta}$
30	20	$R^{-6}\cdot\frac{5}{4}(21(3r_z^{a3}-r_z^a)r_z^{b2} + 6(7r_z^{a2}-1)r_z^b c_{zz} - 7r_z^{a3} + 3r_z^a + 6r_z^a c_{zz}^2)$
30	21c	$R^{-6}\cdot\frac{5}{2}\sqrt{3}(7(3r_z^{a3}-r_z^a)r_x^b r_z^b + (7r_z^{a2}-1)(r_x^b c_{zz} + r_z^b c_{zx}) + 2r_z^a c_{zx}c_{zz})$
30	21s	$R^{-6}\cdot\frac{5}{2}\sqrt{3}(7(3r_z^{a3}-r_z^a)r_y^b r_z^b + (7r_z^{a2}-1)(r_y^b c_{zz} + r_z^b c_{zy}) + 2r_z^a c_{zy}c_{zz})$
30	22c	$R^{-6}\cdot\frac{5}{4}\sqrt{3}(21r_z^{a3} - 7r_z^a)(r_x^{b2}-r_y^{b2}) + 2r_z^a(c_{zx}^2 - c_{zy}^2))$
		$+2(7r_z^{a2}-1)(r_x^b c_{zx} - r_y^b c_{zy})$
30	22s	$R^{-6}\cdot\frac{5}{2}\sqrt{3}(7(3r_z^{a3}-r_z^a)r_x^b r_y^b + (7r_z^{a2}-1)(r_x^b c_{zy} + r_y^b c_{zx}) + 2r_z^a c_{zx}c_{zy})$

molecule B which, in the body-fixed system of molecule A, takes the form $\hat{R}_a^{-1}\boldsymbol{R}$:

$$I_{l_1\kappa_1}(\hat{R}_a^{-1}\boldsymbol{R} + \hat{R}_a^{-1}\hat{R}_b\boldsymbol{r}_b) = \sum_{l_2=0}^{\infty}\frac{1}{l_2!}(\hat{R}_a^{-1}\hat{R}_b\boldsymbol{r}_b\cdot\nabla_{\hat{R}_a^{-1}\boldsymbol{R}})^{l_2}I_{l_1\kappa_1}(\hat{R}_a^{-1}\boldsymbol{R}) \tag{13}$$

$$= \sum_{l_2=0}^{\infty}\frac{1}{l_2!}(\boldsymbol{r}_b\cdot\nabla_{\hat{R}_b^{-1}\boldsymbol{R}})^{l_2}I_{l_1\kappa_1}(\hat{R}_a^{-1}\boldsymbol{R}). \tag{14}$$

For $\boldsymbol{R}\neq 0$ the functions I_{lk} satisfy Laplace's equation, $\Delta I_{lk}(\boldsymbol{R}) = 0$; therefore the

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Table 1. *Continued*

t	u	$4\pi\epsilon_0 T^{ab}_{tu}$
31c	20	$R^{-6}\cdot\frac{5}{8}\sqrt{6}(63r^a_x r^{a2}_z r^{b2}_z - 7r^a_x r^{a2}_z - 7r^a_x r^{b2}_z + 28r^a_x r^a_z r^b_z c_{zz}$
		$+14r^{a2}_z r^b_z c_{xz} + r^a_x - 2r^b_z c_{xz} + 2r^a_x c^2_{zz} + 4r^a_z c_{xz} c_{zz})$
31c	21c	$R^{-6}\cdot\frac{5}{4}\sqrt{2}(7(9r^{a2}_z - 1)r^a_x r^b_x r^b_z + 14r^a_x r^a_z (r^b_x c_{zz} + r^b_z c_{zx})$
		$+(7r^{a2}_z - 1)(r^b_x c_{xz} + r^b_z c_{xx}) + 2r^a_x c_{zx} c_{zz} + 2r^a_z (c_{xx} c_{zz} + c_{xz} c_{zx}))$
31c	21s	$R^{-6}\cdot\frac{5}{4}\sqrt{2}(7(9r^{a2}_z - 1)r^a_x r^b_y r^b_z + 14r^a_x r^a_z (r^b_y c_{zz} + r^b_z c_{zy})$
		$+(7r^{a2}_z - 1)(r^b_y c_{xz} + r^b_z c_{xy}) + 2r^a_x c_{zy} c_{zz} + 2r^a_z (c_{xy} c_{zz} + c_{xz} c_{zy}))$
31c	22c	$R^{-6}\cdot\frac{5}{8}\sqrt{2}(7r^a_x (9r^{a2}_z - 1)(r^{b2}_x - r^{b2}_y) + 14r^{a2}_z (r^b_x c_{xx} - r^b_y c_{xy})$
		$+28r^a_x r^a_z (r^b_x c_{zx} - r^b_y c_{zy}) + 4r^a_z c_{xx} c_{zx} - 4r^a_z c_{xy} c_{zy}$
		$-2r^b_x c_{xx} + 2r^b_y c_{xy} + 2r^a_x c^2_{zx} - 2r^a_x c^2_{zy})$
31c	22s	$R^{-6}\cdot\frac{5}{4}\sqrt{2}(7r^a_x (9r^{a2}_z - 1)r^b_x r^b_y + 14r^a_x r^a_z (r^b_x c_{zy} + r^b_y c_{zx})$
		$+(7r^{a2}_z - 1)(r^b_x c_{xy} + r^b_y c_{xx}) + 2r^a_x c_{zx} c_{zy} + 2r^a_z (c_{xx} c_{zy} + c_{xy} c_{zx}))$
31s	20	$R^{-6}\cdot\frac{5}{8}\sqrt{6}(63r^a_y r^{a2}_z r^{b2}_z - 7r^a_y r^{a2}_z - 7r^a_y r^{b2}_z + 28r^a_y r^a_z r^b_z c_{zz}$
		$+14r^{a2}_z r^b_z c_{yz} + r^a_y - 2r^b_z c_{yz} + 2r^a_y c^2_{zz} + 4r^a_z c_{yz} c_{zz})$
31s	21c	$R^{-6}\cdot\frac{5}{4}\sqrt{2}(7r^a_y (9r^{a2}_z - 1)r^b_x r^b_z + 14r^a_y r^a_z (r^b_x c_{zz} + r^b_z c_{zx})$
		$+7(r^{a2}_z - 1)(r^b_x c_{yz} + r^b_z c_{yx}) + 2r^a_y c_{zx} c_{zz} + 2r^a_z (c_{yx} c_{zz} + c_{yz} c_{zx}))$
31s	21s	$R^{-6}\cdot\frac{5}{4}\sqrt{2}(7r^a_y (9r^{a2}_z - 1)r^b_y r^b_z + 14r^a_y r^a_z (r^b_y c_{zz} + r^b_z c_{zy})$
		$+7(r^{a2}_z - 1)(r^b_y c_{yz} + r^b_z c_{yy}) + 2r^a_y c_{zy} c_{zz} + 2r^a_z (c_{yy} c_{zz} + c_{yz} c_{zy}))$
31s	22c	$R^{-6}\cdot\frac{5}{8}\sqrt{2}(7r^a_y (9r^{a2}_z - 1)(r^{b2}_x - r^{b2}_y) + 2(7r^{a2}_z - 1)(r^b_x c_{yx} - r^b_y c_{yy})$
		$+28r^a_y r^a_z (r^b_x c_{zx} - r^b_y c_{zy}) + 2r^a_y (c^2_{zx} - c^2_{zy}) + 4r^a_z (c_{yx} c_{zx} - c_{yy} c_{zy}))$
31s	22s	$R^{-6}\cdot\frac{5}{4}\sqrt{2}(7r^a_y (9r^{a2}_z - 1)r^b_x r^b_y + 14r^a_y r^a_z (r^b_x c_{zy} + r^b_y c_{zx})$
		$+(7r^{a2}_z - 1)(r^b_x c_{yy} + r^b_y c_{yx}) + 2r^a_y c_{zx} c_{zy} + 2r^a_z (c_{yx} c_{zy} + c_{yy} c_{zx}))$
32c	20	$R^{-6}\cdot\frac{1}{4}\sqrt{15}(7(r^{a2}_x - r^{a2}_y)(9r^{a2}_z r^{b2}_z - r^{a2}_z + 2r^{b2}_z c_{zz}) + 28(r^a_x c_{xz} - r^a_y c_{yz}) r^a_z r^b_z$
		$+4r^a_x c_{xz} c_{zz} - 4r^a_y c_{yz} c_{zz} + 2r^a_z (c^2_{xz} - c^2_{yz}))$

Taylor expansion can be replaced by an equivalent expansion in spherical tensors [5, 8]:

$$I_{l_1\kappa_1}(\hat{R}_a^{-1}\boldsymbol{R} + \hat{R}_a^{-1}\hat{R}_b\boldsymbol{r}_b) = \sum_{l_2=0}^{\infty}\sum_{\kappa_2}\frac{1}{(2l_2-1)!!}R_{l_2\kappa_2}(\boldsymbol{r}_b)\cdot R_{l_2\kappa_2}(\nabla_{\hat{R}_b^{-1}\boldsymbol{R}})\cdot I_{l_1\kappa_1}(\hat{R}_a^{-1}\boldsymbol{R}), \tag{15}$$

where we have introduced the operators $R_{l\kappa}(\nabla)$, which are obtained by replacing in the real solid harmonics $R_{l\kappa}(\boldsymbol{r})$ the components x, y and z of $\boldsymbol{r}$ by the components of ∇ (for a more rigorous definition of these operators and the definition of $(2n-1)!!$ see the appendix).

Substituting equation (15) in (7) evaluating the integral we find the required

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Table 1. *Continued*

t	u	$4\pi\epsilon_0 T^{ab}_{tu}$
$32c$	$21c$	$R^{-6}\cdot\frac{1}{2}\sqrt{5}(63r^a_z(r^{a2}_x-r^{a2}_y)r^b_x r^b_z+7(r^{a2}_x-r^{a2}_y)(r^b_x c_{zz}+r^b_z c_{zx})$
		$+14r^a_x r^a_z(r^b_x c_{xz}+r^b_z c_{xx})-14r^a_y r^a_z(r^b_x c_{yz}+r^b_z c_{yx})$
		$+2r^a_x(c_{xx}c_{zz}+c_{xz}c_{zx})-2r^a_y(c_{yx}c_{zz}+c_{yz}c_{zx})+2r^a_z(c_{xx}c_{xz}-c_{yx}c_{yz}))$
$32c$	$21s$	$R^{-6}\cdot\frac{1}{2}\sqrt{5}(63(r^{a2}_x-r^{a2}_y)r^a_z r^b_y r^b_z+7(r^{a2}_x-r^{a2}_y)(r^b_y c_{zz}+r^b_z c_{zy})$
		$+14r^a_x r^a_z(r^b_y c_{xz}+r^b_z c_{xy})-14r^a_y r^a_z(r^b_y c_{yz}+r^b_z c_{yy})$
		$+2r^a_x(c_{xy}c_{zz}+c_{xz}c_{zy})-2r^a_y(c_{yy}c_{zz}+c_{yz}c_{zy})+2r^a_z(c_{xy}c_{xz}-c_{yy}c_{yz}))$
$32c$	$22c$	$R^{-6}\cdot\frac{1}{4}\sqrt{5}(63r^a_z(r^{a2}_x-r^{a2}_y)(r^{b2}_x-r^{b2}_y)+14(r^{a2}_x-r^{a2}_y)(r^b_x c_{zx}-r^b_y c_{zy})$
		$+28r^a_z(r^a_x r^b_x c_{xx}-r^a_x r^b_y c_{xy}-r^a_y r^b_x c_{yx}+r^a_y r^b_y c_{yy})-4r^a_y(c_{yx}c_{zx}-c_{yy}c_{zy})$
		$+4r^a_x(c_{xx}c_{zx}-c_{xy}c_{zy})+2r^a_z(c^2_{xx}-c^2_{xy}-c^2_{yx}+c^2_{yy}))$
$32c$	$22s$	$R^{-6}\cdot\frac{1}{2}\sqrt{5}(63(r^{a2}_x-r^{a2}_y)r^a_z r^b_x r^b_y+7(r^{a2}_x-r^{a2}_y)(r^b_x c_{zy}+r^b_y c_{zx})$
		$+14r^a_x r^a_z(r^b_x c_{xy}+r^b_y c_{xx})-14r^a_y r^a_z(r^b_x c_{yy}+r^b_y c_{yx})$
		$+2r^a_x(c_{xx}c_{zy}+c_{xy}c_{zx})-2r^a_y(c_{yx}c_{zy}+c_{yy}c_{zx})+2r^a_z(c_{xx}c_{xy}-c_{yx}c_{yy}))$
$32s$	20	$R^{-6}\cdot\frac{1}{2}\sqrt{15}(63r^a_x r^a_y r^a_z r^{b2}_z-7r^a_x r^a_y r^a_z+14r^a_x r^a_y r^b_z c_{zz}$
		$+14r^a_z r^b_z(r^a_x c_{yz}+r^a_y c_{xz})+2(r^a_x c_{yz}+r^a_y c_{xz})c_{zz}+2r^a_z c_{xz}c_{yz})$
$32s$	$21c$	$R^{-6}\cdot\sqrt{5}(63r^a_x r^a_y r^a_z r^b_x r^b_z+7r^a_x r^a_y(r^b_x c_{zz}+r^b_z c_{zx})$
		$+7r^a_x r^a_z(r^b_x c_{yz}+r^b_z c_{yx})+7r^a_y r^a_z(r^b_x c_{xz}+r^b_z c_{xx})$
		$+r^a_x(c_{yx}c_{zz}+c_{yz}c_{zx})+r^a_y(c_{xx}c_{zz}+c_{xz}c_{zx})+r^a_z(c_{xx}c_{yz}+c_{xz}c_{yx}))$
$32s$	$21s$	$R^{-6}\cdot\sqrt{5}(63r^a_x r^a_y r^a_z r^b_y r^b_z+7r^a_x r^a_y(r^b_y c_{zz}+r^b_z c_{zy})$
		$+7r^a_x r^a_z(r^b_y c_{yz}+r^b_z c_{yy})+7r^a_y r^a_z(r^b_y c_{xz}+r^b_z c_{xy})$
		$+r^a_x(c_{yy}c_{zz}+c_{yz}c_{zy})+r^a_y(c_{xy}c_{zz}+c_{xz}c_{zy})+r^a_z(c_{xy}c_{yz}+c_{xz}c_{yy}))$
$32s$	$22c$	$R^{-6}\cdot\frac{1}{2}\sqrt{5}(63r^a_x r^a_y r^a_z(r^{b2}_x-r^{b2}_y)+14r^a_x r^a_y(r^b_x c_{zx}-r^b_y c_{zy})$
		$+14r^a_x r^a_z(r^b_x c_{yx}-r^b_y c_{yy})+14r^a_y r^a_z(r^b_x c_{xx}-r^b_y c_{xy})+2r^a_x(c_{yx}c_{zx}-c_{yy}c_{zy})$
		$+2r^a_y(c_{xx}c_{zx}-c_{xy}c_{zy})+2r^a_z(c_{xx}c_{yx}-c_{xy}c_{yy}))$

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expression for the interaction tensors:

$$U_{\mathrm{es}}=\frac{1}{4\pi\epsilon_0}\sum_{l_1=0}^{\infty}\sum_{\kappa_1}\sum_{l_2=0}^{\infty}\sum_{\kappa_2}\int\rho^{\mathrm{B}}_{\mathrm{m}}(\boldsymbol{r}_{\mathrm{b}})\cdot R_{l_2\kappa_2}(\boldsymbol{r}_{\mathrm{b}})\,\mathrm{d}^3r_{\mathrm{b}} \tag{16}$$

$$\times\frac{1}{(2l_2-1)!!}R_{l_2\kappa_2}(\nabla_{\hat{R}_{\mathrm{b}}^{-1}\boldsymbol{R}})\cdot I_{l_1\kappa_1}(\hat{R}_{\mathrm{a}}^{-1}\boldsymbol{R})\cdot Q^{\mathrm{A}}_{l_1\kappa_1}$$

$$=\frac{1}{4\pi\epsilon_0}\sum_{l_1=0}^{\infty}\sum_{\kappa_1}\sum_{l_2=0}^{\infty}\sum_{\kappa_2}Q^{\mathrm{A}}_{l_1\kappa_1}\cdot\left(\frac{1}{(2l_2-1)!!}R_{l_2\kappa_2}(\nabla_{\hat{R}_{\mathrm{b}}^{-1}\boldsymbol{R}})I_{l_1\kappa_1}(\hat{R}_{\mathrm{a}}^{-1}\boldsymbol{R})\right)\cdot Q^{\mathrm{B}}_{l_2\kappa_2}.$$

$$=\sum_{l_1=0}^{\infty}\sum_{\kappa_1}\sum_{l_2=0}^{\infty}\sum_{\kappa_2}Q^{\mathrm{A}}_{l_1\kappa_1}\cdot T^{\mathrm{AB}}_{l_1\kappa_1 l_2\kappa_2}\cdot Q^{\mathrm{B}}_{l_2\kappa_2}, \tag{17}$$

Table 1. *Continued*

t	u	$4\pi\epsilon_0 T^{ab}_{tu}$
32*s*	22*s*	$R^{-6}\cdot\sqrt{5}(63r_x^a r_y^a r_z^a r_x^b r_y^b + 7r_x^a r_y^a(r_x^b c_{zy} + r_y^b c_{zx}) + 7r_x^a r_z^a(r_x^b c_{yy} + r_y^b c_{yx})$ $+7r_y^a r_z^a(r_x^b c_{xy} + r_y^b c_{xx}) + r_x^a(c_{yx}c_{zy} + c_{yy}c_{zx}) + r_y^a(c_{xx}c_{zy} + c_{xy}c_{zx})$ $+r_z^a(c_{xx}c_{yy} + c_{xy}c_{yx}))$
33*c*	20	$R^{-6}\cdot\frac{1}{8}\sqrt{10}(63r_x^{a3}r_z^{b2} - 189r_x^a r_y^{a2} r_z^{b2} - 7r_x^{a3} + 21r_x^a r_y^{a2} + 42r_x^{a2} r_z^b c_{xz}$ $-84r_x^a r_y^a r_z^b c_{yz} - 42r_y^{a2} r_z^b c_{xz} + 6r_x^a c_{xz}^2 - 6r_x^a c_{yz}^2 - 12r_y^a c_{xz}c_{yz})$
33*c*	21*c*	$R^{-6}\cdot\frac{1}{4}\sqrt{30}(21r_x^a(r_x^{a2} - 3r_y^{a2})r_x^b r_z^b + 7(r_x^{a2} - r_y^{a2})(r_x^b c_{xz} + r_z^b c_{xx})$ $-14r_x^a r_y^a(r_x^b c_{yz} + r_z^b c_{yx}) + 2r_x^a(c_{xx}c_{xz} - c_{yx}c_{yz}) - 2r_y^a(c_{xx}c_{yz} + c_{xz}c_{yx}))$
33*c*	21*s*	$R^{-6}\cdot\frac{1}{4}\sqrt{30}(21r_x^a(r_x^{a2} - 3r_y^{a2})r_y^b r_z^b + 7(r_x^{a2} - r_y^{a2})(r_y^b c_{xz} + r_z^b c_{xy})$ $-14r_x^a r_y^a(r_y^b c_{yz} + r_z^b c_{yy}) + 2r_x^a(c_{xy}c_{xz} - c_{yy}c_{yz}) - 2r_y^a(c_{xy}c_{yz} + c_{xz}c_{yy}))$
33*c*	22*c*	$R^{-6}\cdot\frac{1}{8}\sqrt{30}(21(3r_y^{a2} - r_x^{a2})r_x^a(r_y^{b2} - r_x^{b2}) + 14(r_x^{a2} - r_y^{a2})(r_x^b c_{xx} - r_y^b c_{xy})$ $+28r_x^a r_y^a(r_y^b c_{yy} - r_x^b c_{yx}) + 2r_x^a(c_{xx}^2 - c_{xy}^2 - c_{yx}^2 + c_{yy}^2) + 4r_y^a(c_{xy}c_{yy} - c_{xx}c_{yx}))$
33*c*	22*s*	$R^{-6}\cdot\frac{1}{4}\sqrt{30}(21r_x^a(r_x^{a2} - 3r_y^{a2})r_x^b r_y^b + 7(r_x^{a2} - r_y^{a2})(r_x^b c_{xy} + r_y^b c_{xx})$ $-14r_x^a r_y^a(r_x^b c_{yy} - r_y^b c_{yx}) + 2r_x^a(c_{xx}c_{xy} - c_{yx}c_{yy}) - 2r_y^a(c_{xx}c_{yy} + c_{xy}c_{yx}))$
33*s*	20	$R^{-6}\cdot\frac{1}{8}\sqrt{10}(189r_x^{a2}r_y^a r_z^{b2} - 63r_y^{a3}r_z^{b2} - 21r_x^{a2}r_y^a + 7r_y^{a3}$ $+42(r_x^{a2} - r_y^{a2})r_y^b c_{yz} + 84r_x^a r_y^a r_z^b c_{xz} + 12r_x^a c_{xz}c_{yz} + 6r_y^a(c_{xz}^2 - c_{yz}^2))$
33*s*	21*c*	$R^{-6}\cdot\frac{1}{4}\sqrt{30}(21(3r_x^{a2} - r_y^{a2})r_y^a r_x^b r_z^b + 7(r_x^{a2} - r_y^{a2})(r_x^b c_{yz} + r_z^b c_{yx})$ $+14r_x^a r_y^a(r_x^b c_{xz} + r_z^b c_{xx}) + 2r_x^a(c_{xx}c_{yz} + c_{xz}c_{yx}) + 2r_y^a(c_{xx}c_{xz} - c_{yx}c_{yz}))$
33*s*	21*s*	$R^{-6}\cdot\frac{1}{4}\sqrt{30}(21(3r_x^{a2} - r_y^{a2})r_y^a r_x^b r_z^b + 7(r_x^{a2} - r_y^{a2})(r_y^b c_{yz} + r_z^b c_{yy})$ $+14r_x^a r_y^a(r_y^b c_{xz} + r_z^b c_{xy}) + 2r_x^a(c_{xy}c_{yz} + c_{xz}c_{yy}) + 2r_y^a(c_{xy}c_{xz} - c_{yy}c_{yz}))$
33*s*	22*c*	$R^{-6}\cdot\frac{1}{8}\sqrt{30}(21(3r_x^{a2} - r_y^{a2})r_y^a(r_x^{b2} - r_y^{b2}) + 14(r_x^{a2} - r_y^{a2})(r_x^b c_{yx} - r_y^b c_{yy})$ $+28r_x^a r_y^a(r_x^b c_{xx} - r_y^b c_{xy}) + 4r_x^a(c_{xx}c_{yx} - c_{xy}c_{yy}) + 2r_y^a(c_{xx}^2 - c_{xy}^2 - c_{yx}^2 + c_{yy}^2))$
33*s*	22*s*	$R^{-6}\cdot\frac{1}{4}\sqrt{30}(21(3r_x^{a2} - r_y^{a2})r_y^a r_x^b r_y^b + 7(r_x^{a2} - r_y^{a2})(r_x^b c_{yy} - r_y^b c_{yx})$ $+14r_x^a r_y^a(r_x^b c_{xy} + r_y^b c_{xx}) + 2r_x^a(c_{xx}c_{yy} + c_{xy}c_{yx}) + 2r_y^a(c_{xx}c_{xy} - c_{yx}c_{yy}))$

with

$$T^{AB}_{l_1\kappa_1 l_2\kappa_2} = \frac{1}{4\pi\epsilon_0}\frac{1}{(2l_2-1)!!}R_{l_2\kappa_2}(\hat{R}_b^{-1}\hat{R}_a\nabla_{\hat{R}_a^{-1}\boldsymbol{R}})\cdot I_{l_1\kappa_1}(\hat{R}_a^{-1}\boldsymbol{R}). \tag{18}$$

In this expression for the components of the interaction double-tensors the complete information on the orientation dependence is included in the 3×3 matrices $\hat{R}_a$ and $\hat{R}_b$, so that no Wigner rotation matrices are needed, which make the transformation of spherical higher rank tensors so cumbersome.

By use of the identity $I_{l\kappa}(\boldsymbol{R}) = (-1)^l R_{l\kappa}(\nabla)(1/R)$, equation (18) can be expressed in a form which is more symmetric to the exchange of the labels of molecule A and molecule B:

$$T^{AB}_{l_1\kappa_1 l_2\kappa_2}(R,\Omega_a,\Omega_b) = \frac{1}{4\pi\epsilon_0}\frac{(-1)^{l_1}}{(2l_1-1)!!}\cdot\frac{1}{(2l_2-1)!!}R_{l_2\kappa_2}(\hat{R}_b^{-1}\nabla_{\boldsymbol{R}})R_{l_1\kappa_1}(\hat{R}_a^{-1}\nabla_{\boldsymbol{R}})\frac{1}{R}. \tag{19}$$

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3. Calculation of explicit formulae for components of real spherical interaction tensor

Further simplification of equation (18) can be achieved by expressing the rotated internuclear distance vector and the rotated differential operators in terms of direction cosines and the internuclear distance R. Writing $e_\alpha^{(a)}$ and $e_\beta^{(b)}$ for the unit vectors of the molecule-fixed systems expressed in space-fixed coordinates, the rotation matrices $\hat{R}_a$ are given by

$$\hat{R}_a = (e_x^{(a)}, e_y^{(a)}, e_z^{(a)}) \quad \text{and} \quad \hat{R}_b = (e_x^{(b)}, e_y^{(b)}, e_z^{(b)}). \tag{20}$$

Using this and introducing the unit vector $e_{ab} = \boldsymbol{R}/R$ as well as Stone's notation for the direction cosines $r_\alpha^a = e_\alpha^{(a)} \cdot e_{ab}$ and $c_{\alpha\beta} = e_\beta^{(b)} \cdot e_\alpha^{(a)}$ [4], we obtain

$$(\hat{R}_a^{-1}\boldsymbol{R})_\alpha = R \cdot e_\alpha^{(a)} \cdot e_{ab} = R \cdot r_\alpha^a \tag{21}$$

$$(\nabla_{\hat{R}_a^{-1}\boldsymbol{R}})_\alpha = \frac{\partial}{\partial(R \cdot r_\alpha^a)} \tag{22}$$

$$(\hat{R}_b^{-1}\hat{R}_a)_{\beta\alpha} = e_\beta^{(b)} \cdot e_\alpha^{(a)} = c_{\alpha\beta}. \tag{23}$$

Applying these relations to equation (18) and writing $\boldsymbol{r}^a$ for the unit vector with the components r_α^a and $\hat{c}^T$ for the transposed matrix $c_{\alpha\beta}$, we obtain as the result:

$$T^{AB}_{l_1\kappa_1 l_2\kappa_2} = \frac{1}{4\pi\epsilon_0} \frac{1}{(2l_2-1)!!} \cdot R_{l_2\kappa_2}(\hat{c}^T \cdot \nabla_{R\cdot\boldsymbol{r}^a}) \cdot I_{l_1\kappa_1}(R \cdot \boldsymbol{r}^a). \tag{24}$$

If one also introduces the three direction cosines r_β^b defined by

$$r_\beta^b = -e_\beta^{(b)} \cdot e_{ab} \tag{25}$$

and takes into consideration (by the evaluation of explicit formulae for components of $T_{l_1\kappa_1 l_2\kappa_2}$) that

$$\hat{c}^T \cdot \boldsymbol{r}^a = -\boldsymbol{r}^b \tag{26}$$

and the orthonormality relations

$$\sum_i c_{ik} \cdot c_{il} = \delta_{kl} \tag{27}$$

$$\sum_i c_{ki} \cdot c_{li} = \delta_{kl} \tag{28}$$

one obtains directly compact expressions in terms of the direction cosines. Computer-generated interaction tensors up to 5th rank are given in the table. Real spherical interaction tensors up to the 4th rank have been published previously by Price *et al.* [3] and also by Stone [4]. Apart from misprinted signs in the components $T_{21c,21c}, T_{21c,21s}$ and $T_{21s,21s}$, the expressions in the literature are equivalent to our more symmetric formulae [10].

4. Cartesian and complex spherical orientation-dependent interaction tensors

By the same approach similar equations can be derived for cartesian and complex spherical tensors simply by exchanging the expansion in equations (7) and (15) for the equivalent expansions in cartesian or complex spherical components. As we

believe that the real spherical tensors give the most compact and so the most useful description, we do not describe the derivation of the other ones in detail but present only the final equations. The expression for cartesian tensors is

$$T^{l_1 l_2}_{\alpha\beta\ldots\nu,\alpha'\beta'\ldots\mu'} = \sum_{\alpha''}\sum_{\beta''}\cdots\sum_{\mu''}(-1)^{l_1}\frac{1}{4\pi\epsilon_0}\cdot c^{\mathrm{T}}_{\alpha'\alpha''}\cdot c^{\mathrm{T}}_{\beta'\beta''}\cdot\cdots\cdot c^{\mathrm{T}}_{\mu'\mu''}$$
$$\times \nabla^{\alpha}_{\hat{R}_a^{-1}\boldsymbol{R}}\nabla^{\beta}_{\hat{R}_a^{-1}\boldsymbol{R}}\cdots\nabla^{\nu}_{\hat{R}_a^{-1}\boldsymbol{R}}\nabla^{\alpha''}_{\hat{R}_a^{-1}\boldsymbol{R}}\nabla^{\beta''}_{\hat{R}_a^{-1}\boldsymbol{R}}\cdots\nabla^{\mu''}_{\hat{R}_a^{-1}\boldsymbol{R}}\frac{1}{R}. \tag{29}$$

Using Buckingham's definition [9] for the Cartesian multipoles, we arrive at the electrostatic interaction energy given by

$$U_{\mathrm{es}} = \sum_{\alpha\beta\ldots\nu\alpha'\beta'\ldots\mu'} Q^{(l_1)A}_{\alpha\beta\ldots\nu}\cdot\frac{1}{(2l_1-1)!!}\cdot T^{l_1 l_2}_{\alpha\beta\ldots\nu,\alpha'\beta'\ldots\mu'}\cdot\frac{1}{(2l_2-1)!!}\cdot Q^{(l_2)B}_{\alpha'\beta'\ldots\mu'}. \tag{30}$$

For complex spherical tensors we obtain:

$$T^{\mathrm{AB}}_{l_1 m_1 l_2 m_2} = \frac{1}{4\pi\epsilon_0}\frac{1}{(2l_2-1)!!}R^{(l_2)}_{m_2}(\hat{c}^{\mathrm{T}}\cdot\nabla_{\hat{R}_a^{-1}\boldsymbol{R}})\cdot I^{(l_1)}_{m_1}(\hat{R}_a^{-1}\boldsymbol{R}). \tag{31}$$

Here $R^{(l)}_m$ and $I^{(l)}_k$ are the complex regular and irregular spherical harmonics, respectively.

Appendix

The irreducible spherical differential operators $R^{(l)}_k(\nabla)$ can be defined with the help of the shift operators ∇_+ and L_-, known from quantum mechanics [11]:

$$R^{(l)}_l(\nabla) = (-1)^l\left(\frac{(2l-1)!!}{2l!!}\right)^{1/2}(\nabla_+)^l \tag{A 1}$$

$$[L_-, R^{(l)}_m(\nabla)] = [(l+m)(l-m+1)]^{1/2}R^{(l)}_{m-1}(\nabla), \tag{A 2}$$

where ∇_+ and L_- are defined by

$$\nabla_+ = \left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)$$
$$L_- = \frac{1}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$$

and the double factorials are

$$(2l-1)!! = 1\cdot 3\cdot 5\cdot\cdots\cdot(2l-3)\cdot(2l-1)$$
$$(2l)!! = 2\cdot 4\cdot\cdots\cdot(2l-2)\cdot 2l,$$

with

$$(-1)!! = 1$$
$$0!! = 1.$$

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The real linear combinations are obtained as usually by the transformation:

$$R_{lkc}(\nabla) = \sqrt{\tfrac{1}{2}}[(-1)^k R_k^{(l)}(\nabla) + R_{-k}^{(l)}(\nabla)], \quad \text{with } k > 0 \tag{A 3}$$

$$R_{lks}(\nabla) = -i\sqrt{\tfrac{1}{2}}[(-1)^k R_k^{(l)}(\nabla) - R_{-k}^{(l)}(\nabla)]. \tag{A 4}$$

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