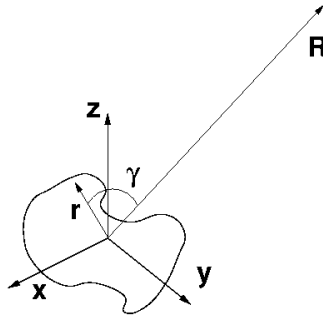


## Chapter 8

# Multipole expansion – spherical harmonics formalism

### 8.1 Potential of a charge distribution



The distance  $|\mathbf{R} - \mathbf{r}|$  can be expressed with the help of the cosine rule

$$(\mathbf{R} - \mathbf{r}) \cdot (\mathbf{R} - \mathbf{r}) = R^2 + r^2 - 2Rr \cos \gamma \quad (8.1)$$

and the Coulomb-kernel can be written in two alternative forms

$$T(\mathbf{R} - \mathbf{r}) = \begin{cases} \frac{1}{R} \left[ 1 + \left( \frac{r}{R} \right)^2 - 2 \left( \frac{r}{R} \right) \cos \gamma \right]^{-1/2} & \text{if } r < R, \\ \frac{1}{r} \left[ 1 + \left( \frac{R}{r} \right)^2 - 2 \left( \frac{R}{r} \right) \cos \gamma \right]^{-1/2} & \text{if } r > R. \end{cases} \quad (8.2)$$

The expression in brackets is just the generator function of the Legendre polynomials

$$(1 + t^2 - 2t \cos \gamma)^{-1/2} = \sum_l^{\infty} P_l(\cos \gamma) t^l \quad |t| < 1 \quad (8.3)$$

The first few Legendre polynomials

$$\begin{aligned}
P_0(x) &= 1 \\
P_1(x) &= x \\
P_2(x) &= \frac{1}{2}(3x^2 - 1) \\
P_3(x) &= \frac{1}{2}(5x^3 - 3x) \\
P_4(x) &= \frac{1}{8}(35x^4 - 30x^2 + 3)
\end{aligned}$$

and at an arbitrary order they can be obtained from the recurrence relation

$$(2l + 1)xP_l = (l + 1)P_{l+1} + lP_{l-1} \quad (8.4)$$

Depending on the space domains, either the first ( $r < R$ ), or the second ( $R < r$ ) form of the generator function can be applied:

$$T(\mathbf{R} - \mathbf{r}) = \begin{cases} \sum_l^\infty \frac{r^l}{R^{l+1}} P_l(\cos \gamma) & \text{if } r < R \\ \sum_l^\infty \frac{R^l}{r^{l+1}} P_l(\cos \gamma) & \text{if } r > R \end{cases} \quad (8.5)$$

The formulae for the two domains of space ( $r < R, r > R$ ) are usually expressed in the following condensed form

$$T(\mathbf{R} - \mathbf{r}) = \sum_{l=0}^\infty \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \gamma) \quad (8.6)$$

Using the addition theorem of spherical harmonics

$$P_l(\cos \gamma) = \left( \frac{4\pi}{2l + 1} \right) \sum_{m=-l}^l Y_{lm}(\omega) Y_{lm}^*(\Omega) \quad (8.7)$$

where  $\omega = (\theta, \phi)$  and  $\Omega = (\Theta, \Phi)$  are the angular components of the polar coordinates of  $\mathbf{r}$  and  $\mathbf{R}$ , respectively.

The (complex) spherical harmonics for  $m \geq 0$

$$Y_{lm}(\omega) = (-)^m \left( \frac{2l + 1}{4\pi} \right) \left( \frac{(l - m)!}{(l + m)!} \right)^{1/2} P_{lm}(\cos \theta) \exp(im\phi) \quad (8.8)$$

and for  $m \leq 0$

$$Y_{l\underline{m}}(\omega) = (-)^m Y_{lm}^*(\omega) \quad (8.9)$$

Here we used the associated Legendre polynomials, that are defined for  $m > 0$  through the derivatives of  $P_l(x)$  as

$$P_{\ell m}(x) = (1 - x^2)^{m/2} \left( \frac{d}{dx} \right)^m P_\ell(x) \quad (8.10)$$

$$\begin{aligned}
P_{00}(\cos \theta) &= 1 \\
P_{10}(\cos \theta) &= \cos \theta \\
P_{11}(\cos \theta) &= \sin \theta \\
P_{20}(\cos \theta) &= \frac{1}{2}(3 \cos^2 \theta - 1) \\
P_{21}(\cos \theta) &= 3 \sin \theta \cos \theta \\
P_{22}(\cos \theta) &= 3 \sin^2 \theta
\end{aligned}$$

Finally, we obtain the spherical harmonics form of the interaction kernel

$$T(\mathbf{R} - \mathbf{r}) = \left( \frac{4\pi}{2l+1} \right) \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{r_{>}^l}{r_{<}^{l+1}} Y_{lm}(\omega) Y_{lm}^*(\Omega) \quad (8.11)$$

### 8.1.1 Potential outside of the charge distribution

If the charge distribution  $\varrho(\mathbf{r})$  vanishes in the points  $R$  where we want to calculate the potential, the condition  $r < R$  is always satisfied

$$V(\mathbf{R}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left( \frac{4\pi}{2\ell+1} \right) Y_{\ell m}^*(\Omega) R^{-\ell-1} \int d\mathbf{r} Y_{\ell m}(\omega) r^{\ell} \varrho(\mathbf{r}) \quad (8.12)$$

Define the modified spherical harmonics

$$C_{\ell m}(\omega) = \left( \frac{4\pi}{2\ell+1} \right)^{1/2} Y_{\ell m}(\omega) \quad (8.13)$$

as well as the regular,  $R_{\ell m}(\mathbf{r})$ , and irregular,  $I_{\ell m}(\mathbf{r})$ , spherical harmonics

$$R_{\ell m}(\mathbf{r}) = r^{\ell} C_{\ell m}(\omega) \quad I_{\ell m}(\mathbf{r}) = r^{-\ell-1} C_{\ell m}(\omega) \quad (8.14)$$

Using these functions, in terms of complex spherical harmonics multipole moments,  $Q_{\ell m}$

$$Q_{\ell m} = \int d\mathbf{r} R_{\ell m}(\mathbf{r}) \varrho(\mathbf{r}) \quad (8.15)$$

the potential becomes

$$V(\mathbf{R}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (-)^m I_{\ell m}(\mathbf{R}) \int d\mathbf{r} R_{\ell m}(\mathbf{r}) \varrho(\mathbf{r}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (-)^m I_{\ell m}(\mathbf{R}) Q_{\ell m} \quad (8.16)$$

It is more practical to use real spherical harmonics instead the complex ones

$$Q_{\ell mc} = \sqrt{\frac{1}{2}} [(-)^m Q_{\ell m} + Q_{\ell \underline{m}}] \quad (8.17)$$

$$Q_{\ell ms} = \sqrt{\frac{1}{2}} [(-)^m Q_{\ell m} - Q_{\ell \underline{m}}] \quad (8.18)$$

Relationship of the real spherical harmonics and Cartesian multipole moments

$Q_{\ell mc/s}$	$\xi_{\alpha\dots\nu}^{(n)}$	$M_{\alpha\dots\nu}^{(n)}$
$Q_{00}$	$q$	$q$
$Q_{10}$	$m_z$	$\mu_z$
$Q_{11c}$	$m_x$	$\mu_x$
$Q_{11s}$	$m_y$	$\mu_y$
$Q_{20}$	$\frac{1}{2}(2Q_{zz} - Q_{xx} - Q_{yy})$	$\Theta_{zz}$
$Q_{21c}$	$\sqrt{3}Q_{xz}$	$\sqrt{\frac{4}{3}}\Theta_{xz}$
$Q_{21s}$	$\sqrt{3}Q_{yz}$	$\sqrt{\frac{4}{3}}\Theta_{yz}$
$Q_{22c}$	$\frac{\sqrt{3}}{2}(Q_{xx} - Q_{yy})$	$\frac{1}{\sqrt{3}}(\Theta_{xx} - \Theta_{yy})$
$Q_{22s}$	$\sqrt{3}Q_{xy}$	$\sqrt{\frac{4}{3}}\Theta_{xy}$

The absolute value of the multipole moment

$$\overline{Q}_\ell^2 = \sum_{m=-\ell}^{\ell} Q_{\ell m} Q_{\ell m}^* = \sum_{\kappa} Q_{\ell \kappa}^2 \quad (8.19)$$

This quantity is invariant with respect to the orientation of the frame.

### 8.1.2 Potential in the overlap region

Take a charge distribution

$$\varrho(\mathbf{r}) = f(\omega)\sigma(r) \quad (8.20)$$

with a radial part, which vanishes only at  $r \rightarrow \infty$ . The general expression of the potential is

$$V(\mathbf{R}) = \sum_{l=0}^{\infty} \left( \frac{4\pi}{2l+1} \right) \int_0^{\infty} dr r^2 \frac{r_{<}^l}{r_{>}^{l+1}} \sigma(r) \sum_{m=-l}^l \int d\omega Y_{lm}(\omega) Y_{lm}^*(\Omega) \quad (8.21)$$

The radial integral should be divided in two parts

$$I(R) = \int_0^R dr r^2 \frac{r^l}{R^{l+1}} \sigma(r) + \int_R^{\infty} dr r^2 \frac{R^l}{r^{l+1}} \sigma(r) \quad (8.22)$$

For instance, take an exponential function (STO)

$$\sigma(r) = r^n e^{-ar} \quad (8.23)$$

Use the integration rules

$$\begin{aligned} \int_0^\infty dr r^n e^{-ar} &= \frac{n!}{a^{n+1}} \\ \int_R^\infty dr r^n e^{-ar} &= \frac{n!}{a^{n+1}} \sum_{k=0}^n \frac{(aR)^k}{k!} e^{-aR} \end{aligned} \quad (8.24)$$

The radial integral

$$I(R) = \frac{n!}{a^{n+1}} \cdot \frac{1}{R^{l+1}} \left[ 1 - \sum_{k=0}^{n+2+l} \frac{(aR)^k}{k!} e^{-aR} + R^{2l+1} \sum_{k=0}^{n+1-l} \frac{(aR)^k}{k!} e^{-aR} \right] \quad (8.25)$$

For a 1s function ( $l = 0, n = 0$ )

$$\sigma(r) = \frac{\alpha^3}{\pi^3} e^{-2\alpha r} \quad (8.26)$$

the potential

$$V_{(1s)^2}(\mathbf{R}) = \frac{1}{R} \left[ 1 - (1 + \alpha R) e^{-2\alpha R} \right] \quad (8.27)$$

In general, the potential of a charge distribution can be separated to a multipolar and penetration component.

## 8.2 Exact multipolar part of the potential

In quantum chemistry, molecular charge densities are usually developed on Gaussian basis functions

$$\varrho(\mathbf{r}) = \sum_{\alpha} Z_{\alpha} \delta(\mathbf{r} - \mathbf{R}_{\alpha}) - \sum_{\mu\nu} P_{\mu\nu} \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}) \quad (8.28)$$

For this case, the multipolar potential can be exactly evaluated.

Let us consider the  $\chi_{\nu}(\mathbf{r})$  functions as primitive Gaussian functions of the general form

$$\chi(\mathbf{r}) = \mathcal{R}(r) Y_{lm}(\theta, \phi) \quad (8.29)$$

The electronic contribution to the charge density is the sum of two types of terms:

- One-center densities, both basis functions are on the same atomic center

$$\varrho_{\mu\nu}(\mathbf{r}) = \mathcal{R}_\mu(r)\mathcal{R}_\nu(r)Y_{l_\mu m_\mu}(\omega)Y_{l_\nu m_\nu}(\omega) \quad (8.30)$$

Apply the sum rule (Clebsch-Gordan series)

$$Y_{l_\mu m_\mu}(\omega)Y_{l_\nu m_\nu}(\omega) = \sum_{lm} K_{l_\mu l_\nu l}^{\bar{m}_\mu m_\nu m} Y_{lm}(\omega) \quad (8.31)$$

with

$$|l_\mu - l_\nu| < l < l_\mu + l_\nu \quad \text{and} \quad -m_\mu + m_\nu + m = 0 \quad (8.32)$$

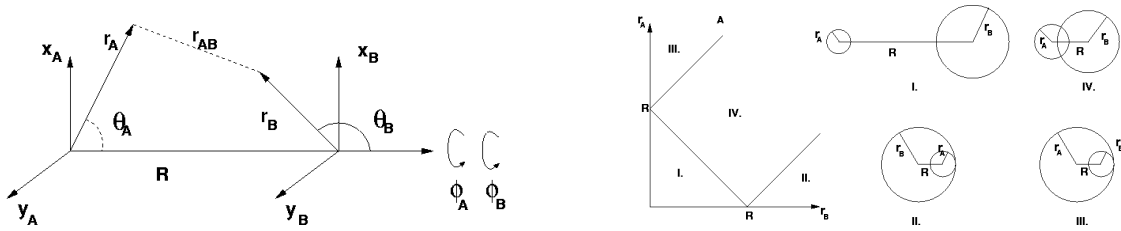
The one-center densities can be written as a finite series of multipolar potentials (maximal order is  $l_\mu + l_\nu$ ) around the natural expansion centre.

- Two-center densities can be handled in an analogous way, by using the Gaussian addition theorem, which leads to the natural expansion centre, the “barycenter”

$$\mathbf{R}_{\mu\nu} = \frac{\alpha_\mu \mathbf{R}_\mu + \alpha_\nu \mathbf{R}_\nu}{\alpha_\mu + \alpha_\nu} \quad (8.33)$$

The multipole expansion wrt to the barycenter is finite, with the highest rank of multipole of  $l_\mu + l_\nu$ .

### 8.3 Buehler-Hirschfelder bipolar expansion



The interaction kernel  $T(\mathbf{r}_{AB})$  is expanded as

$$\frac{1}{r_{AB}} = \sum_{l_A l_B=0}^{\infty} \sum_{m=-l_<}^{l_<} J_{l_A l_B}^{[m]}(\mathbf{r}_A \mathbf{r}_B; \mathbf{R}) Y_{l_A m}(\omega_A) Y_{l_B m}(\omega_B) \quad (8.34)$$

The space is divided on 4 regions and the  $J_{l_A l_B}^{[m]}$  function takes different forms in these regions. Region I. corresponds to the “standard” multipole expansion.

## 8.4 Spherical harmonics expansion of the interaction

One can obtain the bipolar expansion by applying the previously derived result for  $|\mathbf{r}_B - \mathbf{r}_A| < |\mathbf{R}|$

$$\frac{1}{|\mathbf{R} + \mathbf{r}_B - \mathbf{r}_A|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l (-)^m R_{lm}(\mathbf{r}_B - \mathbf{r}_A) I_{lm}(\mathbf{R}) \quad (8.35)$$

According to the addition theorem of regular spherical harmonics

$$\begin{aligned} R_{lm}(\mathbf{r}_B + \mathbf{r}_A) &= \sum_{l_A l_B} \sum_{m_A m_B} \delta_{l_A+l_B, l} (-)^{l-m} \left( \frac{(2l+1)!}{(2l_A)!(2l_B)!} \right)^{1/2} \times \\ &\times \begin{pmatrix} l_A & l_B & l \\ m_A & m_B & m \end{pmatrix} R_{l_A m_A}(\mathbf{r}_A) R_{l_B m_B}(\mathbf{r}_B) \end{aligned} \quad (8.36)$$

where  $\begin{pmatrix} l_A & l_B & l \\ m_A & m_B & m \end{pmatrix}$  a Wigner  $3j$  coefficient.

Use that  $R_{lm}(-\mathbf{r}) = (-)^l R_{lm}(\mathbf{r})$ , the multipole expansion of the interaction energy

$$\begin{aligned} U(\mathbf{R}) &= \sum_{l_A l_B} \sum_{m_A m_B m} (-)^{l_B} \left( \frac{(2l_A + 2l_B + 1)!}{(2l_A)!(2l_B)!} \right)^{1/2} \times \\ &\times \begin{pmatrix} l_A & l_B & l_A + l_B \\ m_A & m_B & m \end{pmatrix} Q_{l_A m_A}^A Q_{l_B m_B}^B I_{l_A+l_B, m}(\mathbf{R}) \end{aligned} \quad (8.37)$$

The multipole moments are expressed in a global coordinate system. Transform the multipoles to a local coordinate system

$$\tilde{Q}_{lk} = \sum_m Q_{lm} D_{mk}^l(\Omega) \quad (8.38)$$

where  $\Omega = (\alpha, \beta, \gamma)$  is the rotation that takes the global axes to the local ones, and  $D_{mk}^l(\Omega)$  are the elements of the (hermitian) Wigner rotation matrices. Inversely, the global multipole components can be written in terms of the local ones

$$Q_{lm} = \sum_k \tilde{Q}_{lk} D_{km}^l(\Omega^{-1}) = \sum_k \tilde{Q}_{lk} [D_{km}^l(\Omega)]^* \quad (8.39)$$

Insert the local-frame multipole moments and define a new orientation-dependent function

$$\begin{aligned} \bar{S}_{l_A l_B j}^{k_A k_B} &= i^{l_A - l_B - j} \left[ \begin{pmatrix} l_A & l_B & j \\ 0 & 0 & 0 \end{pmatrix} \right]^{-1} \times \\ &\times \sum_{m_A m_B m} [D_{k_A m_A}^{l_A}(\Omega_A)]^* [D_{k_B m_B}^{l_B}(\Omega_B)]^* C_{jm}(\theta, \phi) \begin{pmatrix} l_A & l_B & l_A + l_B \\ m_A & m_B & m \end{pmatrix} \end{aligned} \quad (8.40)$$

where  $\theta, \phi$  are the polar angles of the intermolecular vector. In terms of these functions and expanding the Wigner  $3j$  symbols one obtains

$$U(\mathbf{R}) = \sum_{l_A l_B} \sum_{m_A m_B m} \begin{pmatrix} l_A + l_B \\ l_A \end{pmatrix} \tilde{Q}_{l_A m_A}^A \tilde{Q}_{l_B m_B}^B \bar{S}_{l_A l_B l_A + l_B}^{m_A m_B} R^{-l_A - l_B - 1} \quad (8.41)$$

or after transformation to real components

$$U(\mathbf{R}) = \sum_{l_A l_B} \sum_{\kappa_A \kappa_B m} \begin{pmatrix} l_A + l_B \\ l_A \end{pmatrix} \tilde{Q}_{l_A \kappa_A}^A \tilde{Q}_{l_B \kappa_B}^B \bar{S}_{l_A l_B l_A + l_B}^{\kappa_A \kappa_B} R^{-l_A - l_B - 1} \quad (8.42)$$

One can define the spherical analogue of the interaction tensors

$$T_{l_1 \kappa_1, l_2 \kappa_2} = \begin{pmatrix} l_A + l_B \\ l_A \end{pmatrix} \bar{S}_{l_1 l_2 l_1 + l_2}^{\kappa_1 \kappa_2} R^{-l_1 - l_2 - 1} \quad (8.43)$$

and the electrostatic interaction energy (operator) takes the simple form

$$U = \sum_{l_A l_B} \sum_{\kappa_A \kappa_B m} \tilde{Q}_{l_A \kappa_A}^A T_{l_A \kappa_A, l_B \kappa_B} \tilde{Q}_{l_B \kappa_B}^B = \sum_{tu} \tilde{Q}_t^A T_{tu}^{AB} \tilde{Q}_u^B \quad (8.44)$$

with  $t, u = \{l\kappa\}$ .

The  $T$  tensors can be expressed in terms of the unit vectors of the respective local coordinate systems, and the vector  $\mathbf{R}$ .

## 8.5 Interaction tensors between local frame multipoles

Following the derivation of Hättig and Heß (Mol.Phys. 81 (1994) 813), the interaction energy in space-fixed frame

$$U = \iint d\mathbf{r} d\mathbf{s} \frac{\varrho_{\text{SF}}^A(\mathbf{r}) \varrho_{\text{SF}}^B(\mathbf{s})}{|\mathbf{s} - \mathbf{r}|} \quad (8.45)$$

Let us write the rotation matrices from the space-fixed (global) to the molecule-fixed (local) frame as  $\hat{R}(\Omega_A)$  and  $\hat{R}(\Omega_B)$ , where  $\Omega = (\alpha, \beta, \gamma)$  are the Euler angles, and the coordinates

$$\mathbf{r} = \mathbf{A} + \hat{R}(\Omega_A) \mathbf{r}_A \quad \text{and} \quad \mathbf{s} = \mathbf{B} + \hat{R}(\Omega_B) \mathbf{r}_B \quad (8.46)$$

Use the notation  $\mathbf{R} = \mathbf{B} - \mathbf{A}$  and that the length of a vector does not change by rotation

$$|\mathbf{s} - \mathbf{r}| = |\mathbf{R} + \hat{R}(\Omega_B) \mathbf{r}_B - \hat{R}(\Omega_A) \mathbf{r}_A| = |\hat{R}^{-1}(\Omega_A) \mathbf{R} + \hat{R}^{-1}(\Omega_A) \hat{R}(\Omega_B) \mathbf{r}_B - \mathbf{r}_A| \quad (8.47)$$



Electrostatic energy in molecule-fixed charge distributions

$$\begin{aligned}
U &= \iint d\mathbf{r}_A d\mathbf{r}_B \frac{\varrho_{\text{MF}}^A(\mathbf{r}_A) \varrho_{\text{MF}}^B(\mathbf{r}_B)}{|\hat{R}^{-1}(\Omega_A) \mathbf{R} + \hat{R}^{-1}(\Omega_A) \hat{R}(\Omega_B) \mathbf{r}_B - \mathbf{r}_A|} = \\
&= \sum_{l_1}^{\infty} \sum_{\kappa_1} Q_{l_1 \kappa_1}^A \cdot \int d\mathbf{r}_B I_{l_1 \kappa_1}(\hat{R}^{-1}(\Omega_A) \mathbf{R} + \hat{R}^{-1}(\Omega_A) \hat{R}(\Omega_B) \mathbf{r}_B) \cdot \varrho_{\text{MF}}^B(\mathbf{r}_B)
\end{aligned} \tag{8.48}$$

The irregular spherical harmonics can be expanded in Taylor series

$$\begin{aligned}
I_{l_1 \kappa_1}(\hat{R}_A^{-1} \mathbf{R} + \hat{R}_A^{-1} \hat{R}_B \mathbf{r}_B) &= \\
&= \sum_{l_2=0}^{\infty} \frac{1}{l_2!} (\hat{R}_A^{-1} \hat{R}_B \mathbf{r}_B \cdot \nabla_{\hat{R}_A^{-1} \mathbf{R}})^{l_2} \cdot I_{l_1 \kappa_1}(\hat{R}_A^{-1} \mathbf{R}) = \\
&= \sum_{l_2=0}^{\infty} \frac{1}{l_2!} (\mathbf{r}_B \cdot \nabla_{\hat{R}_B^{-1} \mathbf{R}})^{l_2} \cdot I_{l_1 \kappa_1}(\hat{R}_A^{-1} \mathbf{R})
\end{aligned} \tag{8.49}$$

and in terms of spherical tensors as

$$\begin{aligned}
I_{l_1 \kappa_1}(\hat{R}_A^{-1} \mathbf{R} + \hat{R}_A^{-1} \hat{R}_B \mathbf{r}_B) &= \\
&= \sum_{l_2=0}^{\infty} \sum_{\kappa_2} \frac{1}{(2l_2 - 1)!!} R_{l_2 \kappa_2}(\mathbf{r}_B) \cdot R_{l_2 \kappa_2}(\nabla_{\hat{R}_B^{-1} \mathbf{R}}) \cdot I_{l_1 \kappa_1}(\hat{R}_A^{-1} \mathbf{R})
\end{aligned} \tag{8.50}$$

Using the identity  $I_{l\kappa}(\mathbf{R}) = (-)^l R_{l\kappa}(\nabla)(1/R)$ , the interaction energy becomes

$$U = \sum_{l_1}^{\infty} \sum_{\kappa_1} \sum_{l_2}^{\infty} \sum_{\kappa_2} Q_{l_1 \kappa_1}^A \cdot Q_{l_2 \kappa_2}^B \cdot T_{l_1 \kappa_1 l_2 \kappa_2}^{AB} \tag{8.51}$$

with  $T_{l_1 \kappa_1 l_2 \kappa_2}^{AB}$  interaction tensor

$$T_{l_1 \kappa_1 l_2 \kappa_2}^{AB}(R, \Omega_A, \Omega_B) = \frac{(-)^{l_1}}{(2l_1 - 1)!!} \cdot \frac{1}{(2l_2 - 1)!!} R_{l_2 \kappa_2}(\hat{R}_B^{-1} \nabla \mathbf{R}) R_{l_1 \kappa_1}(\hat{R}_A^{-1} \nabla \mathbf{R}) \frac{1}{R} \tag{8.52}$$

The rotated internuclear vector and the rotated differential operators can be expressed in terms of direction cosines and the internuclear distance  $R$ . The rotation matrices can be written in terms of the unit vectors of the molecule fixed frame in the space-fixed system

$$\hat{R}_A = (\mathbf{e}_x^{(A)}, \mathbf{e}_y^{(A)}, \mathbf{e}_z^{(A)}) \quad \text{and} \quad \hat{R}_B = (\mathbf{e}_x^{(B)}, \mathbf{e}_y^{(B)}, \mathbf{e}_z^{(B)})$$

the intermolecular unit vector,  $\mathbf{e}_{AB} = \mathbf{R}/R$  and the direction cosines,  $r_{\alpha}^A = \mathbf{e}_{\alpha}^{(A)} \cdot \mathbf{e}_{AB}$  and

$$c_{\alpha\beta} = \mathbf{e}_{\beta}^{(B)} \cdot \mathbf{e}_{\alpha}^{(A)}.$$

For instance

$$\begin{aligned} T_{20,00} &= \frac{1}{2}(3r_\alpha^{A^2} - 1)R^{-3} \\ T_{1\alpha,1\beta} &= (3r_\alpha^A r_\beta^B + c_{\alpha\beta})R^{-3} \end{aligned} \tag{8.53}$$

Computation of the general expressions in both cartesian and spherical tensors are quite costly and scale as  $L^6$ , where  $L$  is the order of  $1/R$  expansion. Using an intermediate coordinate transformation, Hättig derived general recurrence relations, which scale as  $L^4$  (CPL, 260(1996)341).

