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On the calculation of derivatives for Coulomb-type interaction energies and general anisotropic pair potentials

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Abstract

We derive efficient algorithms for the derivatives, in particular the forces, torques and the Hessian, for Coulomb-type interactions and for general anisotropic pair potentials. We use spherical tensor techniques and an intermediate transformation to a quasi-internal coordinate system, proposed recently to obtain a factorization of the multipole interaction tensors. By these means we obtain a unified approach to the derivatives at small extra computational cost to the energy calculation. For the special case of an electrostatic interaction the computational cost scales for a system of N molecules through rank L in the multipole expansion as $N^2 \times \mathcal{O}(L^3)$ for both the energy and its derivatives. © 1997 Elsevier Science B.V.

1. Introduction

Reliable intermolecular potentials for molecules that interact through weak Van der Waals forces, for example, electrostatic, induction or dispersion forces, require an accurate description of the anisotropic part of the potential provided, in general, only by an ansatz with anisotropic site–site interaction functions using an expansion in Cartesian or spherical tensor components [1,2]. This is particularly important for long-range electrostatic and induction interactions which for neutral molecules are purely anisotropic. A qualitatively correct description of these interactions is normally not obtained if the multipole expansion, which is the basis for these parts of the potential, is truncated before the quadrupole terms and often even octopole and hexadecapole terms have to be included [3,4].

However, in many cases also the short-range repulsion originating from exchange, overlap and Pauli exclusion effects cannot be described using only isotropic atom–atom potentials. Well-documented examples of the importance of the anisotropic terms in atom–atom repulsion potentials are the crystal structures of molecules containing chlorine atoms [5], especially Cl_2, which could not be modelled with isotropic atom–atom potentials.

Although these difficulties are well known and the use of anisotropic interaction functions is standard in studies on the potentials and the spectra of Van der Waals dimers, most molecular dynamics studies on condensed phases are still carried out using isotropic site–site potentials supplemented by point charges at off-atom sites to imitate the anisotropy of the electrostatic interaction. A general ansatz for site–site potentials allowing for higher rank anisotropy contributions is believed to be too complicated in the implementation and too expensive for most applications of molecular dynamics simulations.

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Work has recently been published by several authors on the derivation of efficient algorithms for Cartesian and spherical multipole interaction tensors that scale through order L in the multipole expansion as L^4 [6–8]. In Ref. [8] an intermediate transformation to a coordinate system with the z-axes parallel to the intermolecular distance vector has been introduced to obtain a factorization of the so-called S functions and the orientation-dependent spherical multipole interaction tensors. In combination with recurrence relations for the Wigner rotation matrices this factorization made it possible to devise new open-ended algorithms for the electrostatic, induction and dispersion interactions which scale for a system with N rigid molecules through order L in the multipole expansion only as $N^2 \times \mathcal{O}(L^3)$, $N^2 \times \mathcal{O}(L^3) + N \times \mathcal{O}(L^4)$ and $N^2 \times \mathcal{O}(L^5)$ respectively. Thus now the necessary techniques are available to calculate the energies resulting from these Coulomb-type interactions efficiently through high orders in the multipole expansions.

However, not much work has been published that focuses on the calculation of derivatives for these energies which are required for the forces and torques and the Hessian needed in molecular dynamics simulations and for the search and classification of stationary points on the potential hypersurface. In Ref. [9] Price et al. derived explicit formulae for the forces and torques arising from electrostatic interactions up to fifth order in $1/R$ using the framework of orientation-dependent spherical interaction tensors. This derivation has been revised recently by Popelier and Stone [10] using a more rigorous and unified approach for the terms arising from what these authors called the "lower part of the chain rule". However, because these authors start from explicit expressions for each of the components of the multipole interaction tensor in terms of 16 direction cosines as intermediate variables, the results of this derivation are complicated and lengthy, requiring for each interacting pair of molecules the evaluation of 16 derivatives for the calculation of the 6 independent contributions to the forces and torques and no less than 136 second derivatives for the 21 independent contributions to the Hessian.

In this Letter we use the quasi-internal coordinate system devised in Ref. [8] to obtain a parametrization of the orientation-dependent interaction functions in which only a minimum number of 6 first and 21 second derivatives have to be calculated.

2. General anisotropic pair potentials in the real spherical double tensor formalism

A general anisotropic potential for the interaction between two rigid molecules can be expanded in terms of the so-called S functions, which are defined as linear combinations of Wigner rotation matrices [11–13]:

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

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 molecules and the intermolecular distance vector in an arbitrary global reference frame. The expression in parentheses is a Wigner $3j$ symbol [14], which is chosen so that the result of the summation in Eq. (1) is guaranteed to be a scalar, i.e. invariant with respect to rotation of the reference frame. That this is indeed the case can be verified as follows:

$$\hat{R}\left(\Omega_x^{-1}\right) S^{k_a k_b}_{l_a l_b j}(\Omega_a, \Omega_b, \Omega_{ab}) = S^{k_a k_b}_{l_a l_b j}\left(\hat{R}(\Omega_x)\Omega_a, \hat{R}(\Omega_x)\Omega_b, \hat{R}(\Omega_x)\Omega_{ab}\right) \tag{2}$$

$$= i^{l_a - l_b - j} \sum_{\substack{m_a m_b m \\ m'_a m'_b m'}} D^{(l_a)}_{m_a m'_a}(\Omega_x)^* D^{(l_a)}_{m'_a k_a}(\Omega_a)^* D^{(l_b)}_{m_b m'_b}(\Omega_x)^* D^{(l_b)}_{m'_b k_b}(\Omega_b)^* D^{(j)}_{mm'}(\Omega_x)^* D^{(j)}_{m'0}(\Omega_{ab})^* \begin{pmatrix} l_a & l_b & j \\ m_a & m_b & m \end{pmatrix}, \tag{3}$$

$$= i^{l_a - l_b - j} \sum_{m'_a m'_b m'} D^{(l_a)}_{m'_a k_a}(\Omega_a)^* D^{(l_b)}_{m'_b k_b}(\Omega_b)^* D^{(j)}_{m'0}(\Omega_{ab})^* \times \sum_{m_a m_b m} D^{(l_a)}_{m_a m'_a}(\Omega_x)^* D^{(l_b)}_{m_b m'_b}(\Omega_x)^* D^{(j)}_{mm'}(\Omega_x)^* \begin{pmatrix} l_a & l_b & j \\ m_a & m_b & m \end{pmatrix}, \tag{4}$$

If we insert in Eq. (4) the relation [14]:

$$\sum_{m_a m_b m} D^{(l_a)}_{m_a m'_a}(\Omega) D^{(l_b)}_{m_b m'_b}(\Omega) D^{(j)}_{m m'}(\Omega) \begin{pmatrix} l_a & l_b & j \\ m_a & m_b & m \end{pmatrix} = \begin{pmatrix} l_a & l_b & j \\ m'_a & m'_b & m' \end{pmatrix}, \tag{5}$$

we find the identity, we looked for:

$$\hat{R}(\Omega_x^{-1}) S^{k_a k_b}_{l_a l_b j}(\Omega_a, \Omega_b, \Omega_{ab}) = S^{k_a k_b}_{l_a l_b j}(\Omega_a, \Omega_b, \Omega_{ab}). \tag{6}$$

In addition to invariance with respect to rotations of the reference frame one should also require that the expansion functions for an interaction energy are invariant with respect to an inversion of the entire system. The effect of the inversion operation on a S function is

$$\hat{I} S^{k_a k_b}_{l_a l_b j}(\Omega_a, \Omega_b, \Omega_{ab}) = (-1)^{l_a + l_b + j} S^{k_a k_b}_{l_a l_b j}(\Omega_a, \Omega_b, \Omega_{ab}). \tag{7}$$

Thus ungerade S functions with an odd total rank $l_a + l_b + j$ cannot contribute to an interaction energy, only gerade S functions with an even total rank can contribute to a gerade scalar property. For convenience we renormalize the gerade S functions according to

$$\overline{S}^{k_a k_b}_{l_a l_b j} = S^{k_a k_b}_{l_a l_b j} \times \begin{pmatrix} l_a & l_b & j \\ 0 & 0 & 0 \end{pmatrix}^{-1}. \tag{8}$$

The $\overline{S}$ functions form a complete set for the expansion of anisotropic pair potentials. A general ansatz for a pair potential can be written, for example, as:

$$E^{AB} = \sum_{\substack{n k_a k_b \\ l_a l_b j}} C^{k_a k_b}_{l_a l_b j n} \overline{S}^{k_a k_b}_{l_a l_b j}(\Omega_a, \Omega_b, \Omega_{ab}) G^n_{l_a l_b j}(R), \tag{9}$$

where $C^{k_a k_b}_{l_a l_b j n}$ are system-dependent coefficients and the $G^n_{l_a l_b j}(R)$ are a set of suitable functions for describing the distance dependence of the interaction.

The S functions used in Eqs. (1)–(9) have been defined via the rotation matrices for complex spherical tensors. For most applications it will be more convenient to use real spherical tensors instead of complex ones. The appropriate linear combinations of the interaction functions for real spherical tensor components ${}^r\overline{S}$ are obtained by the transformation:

$${}^r\overline{S}^{\kappa_a \kappa_b}_{l_a l_b j} = \sum_{m_a m_b} X^{(l_a)}_{\kappa_a m_a} X^{(l_b)}_{\kappa_b m_b} \overline{S}^{m_a m_b}_{l_a l_b j} \tag{10}$$

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

$$X^{(l)}_{\kappa,m} = \begin{cases} 1 & \text{for } \kappa = 0, \quad m = 0; \\ \dfrac{(-1)^{|m|}}{\sqrt{2}} & \text{for } \kappa = |m|c, \ m > 0; \\ \dfrac{1}{\sqrt{2}} & \text{for } \kappa = |m|c, \ m < 0; \\ \dfrac{(-1)^{|m|}}{i\sqrt{2}} & \text{for } \kappa = |m|s, \ m > 0; \\ \dfrac{-1}{i\sqrt{2}} & \text{for } \kappa = |m|s, \ m < 0; \\ 0 & \text{else.} \end{cases} \tag{11}$$

As proposed in Ref. [8], the invariance properties of the $\overline{S}$ functions can be used to transform the expressions into a particular coordinate system, in which Eq. (1) becomes especially simple: the coordinate system with the z-axis parallel to the intermolecular distance vector. For this special choice the $D^{(l)}_{m0}(\Omega_{ab})$ become $D^{(l)}_{m0}(0) = \delta_{m0}$ and the expression for the $\overline{S}$ functions takes the form:

$$\overline{S}^{k_a k_b}_{l_a l_b j}(\Omega_a, \Omega_b, \Omega_{ab}) = \overline{S}^{k_a k_b}_{l_a l_b j}(\tilde{\Omega}_a, \tilde{\Omega}_b, 0)$$
$$= i^{l_a - l_b - j} \sum_m D^{(l_a)}_{m k_a}(\tilde{\Omega}_a)^* D^{(l_b)}_{m k_b}(\tilde{\Omega}_b)^* \begin{pmatrix} l_a & l_b & j \\ m & m & 0 \end{pmatrix} \begin{pmatrix} l_a & l_b & j \\ 0 & 0 & 0 \end{pmatrix}^{-1}, \tag{12}$$

where we introduced the short-hand notation $\tilde{\Omega}_a = \hat{R}(\Omega_{ab}^{-1})\Omega_a$ and $\tilde{\Omega}_b = \hat{R}(\Omega_{ab}^{-1})\Omega_b$ for the Euler angles of the molecules A and B in the quasi-internal coordinate system. For the ${}^r\overline{S}$ functions one obtains an analogous equation

$${}^r S^{k_a k_b}_{l_a l_b j}(\tilde{\Omega}_a, \tilde{\Omega}_b, 0) = i^{l_a - l_b - j} \sum_m {}^r D^{(l_a)}_{m k_a}(\tilde{\Omega}_a) {}^r D^{(l_b)}_{m k_b}(\tilde{\Omega}_b) \begin{pmatrix} l_a & l_b & j \\ m & m & 0 \end{pmatrix} \begin{pmatrix} l_a & l_b & j \\ 0 & 0 & 0 \end{pmatrix}^{-1}, \tag{13}$$

where ${}^rD^{(l)}$ are rotation matrices for real spherical tensors [8,15]. The form in which the $\overline{S}$ and ${}^r\overline{S}$ function have been given in Eqs. (12) and (13) is particularly useful, if the coefficients $C^{k_a k_b}_{l_a l_b jn}$ in Eq. (9) can be written as simple products of the properties of the isolated constituents. Then Eqs. (12) and (13) can be used to write the expression for the interaction energy as a product of sparse matrices multiplied by the left and by the right with "vectors" of molecular coefficients. For example, the multipole expanded electrostatic interaction energy then takes the form:

$$E^{AB}_{es}(\tilde{\Omega}_a, \tilde{\Omega}_b, R) = \sum_{\substack{\kappa_a \kappa_b \kappa \\ l_a l_b}} {}^A Q_{l_a \kappa_a} {}^r D^{(l_a)}_{\kappa \kappa_a}(\tilde{\Omega}_a) t^{(l_a, l_b)}_{\kappa}(R) {}^r D^{(l_b)}_{\kappa \kappa_b}(\tilde{\Omega}_b) {}^B Q_{l_b \kappa_b}, \tag{14}$$

where the multipole interaction tensors in this particular coordinate system are given by the simple expression:

$$t^{(l_a, l_b)}_m(R) = R^{-l_a - l_b - 1} \frac{(-1)^{l_b}}{4\pi\epsilon_o} \sqrt{\binom{l_a + l_b}{l_a + m}} \sqrt{\binom{l_a + l_b}{l_a - m}}. \tag{15}$$

Note, that in contrast to Ref. [8] here the R dependence is included in the interaction tensors to obtain later a more compact notation for the derivatives. As shown in Ref. [8], Eq. (14) can be evaluated up to order L in the multipole expansion with computational costs of only $\mathcal{O}(L^3)$, if the Wigner rotation matrices are calculated by means of recurrence relations.

We call the coordinate system with the z-axis parallel to the intermolecular distance vector "quasi-internal", because in this coordinate system the expressions for interaction energies no longer depend on a redundant set of eight angles $(\phi_a, \theta_a, \psi_a, \phi_b, \theta_b, \psi_b, \phi_{ab}, \theta_{ab})$ but only on the six independent angular variables $\tilde{\phi}_a$, $\tilde{\theta}_a$, $\tilde{\psi}_a$, $\tilde{\phi}_b$, $\tilde{\theta}_b$, $\tilde{\psi}_b$, which, together with the distance R, almost form a set of internal coordinates, i.e. a set of variables which does not contain components of the translation or the rotation of the entire complex: $\tilde{\theta}_a$, $\tilde{\psi}_a$, $\tilde{\theta}_b$, $\tilde{\psi}_b$, R and the linear combination $\frac{1}{2}(\tilde{\phi}_a - \tilde{\phi}_b)$ are true internal coordinates, while $\frac{1}{2}(\tilde{\phi}_a + \tilde{\phi}_b)$ describes the rotation of the entire complex about the intermolecular distance vector.

The rotation matrices that enter the S functions in Eqs. (12) and (13) describe the transformation of spherical tensors from the molecule-fixed frames to the quasi-internal coordinate system and vice-versa. Thus within this approach the evaluation of interaction energies is naturally implemented using intermediates in the molecule-fixed and/or quasi-internal coordinate systems, but normally no intermediates will be used that refer to the original global reference frame. This implies that the first derivatives, which as vector properties refer explicitly to a certain coordinate frame, can be evaluated in an efficient way only in either the molecule-fixed or the

quasi-internal coordinate system. These possibilities correspond to two different strategies for the calculation of derivatives of the intermediates used in the energy calculation. In this Letter we focus on the more general formulation that is obtained if the derivatives are taken in the quasi-internal coordinate system.

3. Calculation of derivatives in the quasi-internal coordinate system

To get handy formulae for the derivatives of the rotation matrices we first take a look at the parameterization of the rotation operator, i.e. the operator for which the rotation matrices are the matrix representations in the respective tensor formalism. Using the angular momentum operators in a space-fixed coordinate system,

$$\hat{L}_x = \frac{1}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \qquad \hat{L}_y = \frac{1}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \qquad \hat{L}_z = \frac{1}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right), \tag{16}$$

the rotation operator can be written in terms of the euler angles $\Omega = (\phi, \theta, \psi)$ as [16]:

$$\hat{R}_\Omega = \mathrm{e}^{-i\phi\hat{L}_z} \times \mathrm{e}^{-i\theta\hat{L}_y} \times \mathrm{e}^{-i\psi\hat{L}_z}. \tag{17}$$

For the calculation of derivatives this parametrization is inconvenient, because it defines an explicit order for the three components of the total rotation operation which do not commute, as the angular momentum operators do not commute. Therefore, we partition for the calculation of derivatives the rotation from the molecule-fixed coordinate system to the quasi-internal coordinate system into two subsequent steps: first we rotate from the molecule-fixed coordinate system to an intermediate system by applying $\hat{R}_\Omega^{-1}$ with the fixed angles Ω of the reference geometry, and in a second step we transform from this intermediate system to the quasi-internal coordinate system by a simultaneous rotation through the axes of the rotated system $(x_\Omega, y_\Omega, z_\Omega)$:

$$\hat{R}_\Omega^{-1}(\alpha) = \exp(i\alpha_x\hat{L}_{x_\Omega} + i\alpha_y\hat{L}_{y_\Omega} + i\alpha_z\hat{L}_{z_\Omega})\hat{R}_\Omega^{-1}. \tag{18}$$

The derivatives of the rotation operator and of its inverse with respect to the angles α_ν are then obtained as:

$$\left(\frac{\partial}{\partial\alpha_\nu}\hat{R}_\Omega^{-1}(\alpha)\right)_0 = i\hat{L}_{\nu_\Omega}\,\hat{R}_\Omega^{-1}, \quad \nu = x, y, z, \tag{19}$$

$$\left(\frac{\partial}{\partial\alpha_\nu}\hat{R}_\Omega(\alpha)\right)_0 = -i\hat{R}_\Omega\,\hat{L}_{\nu_\Omega}. \tag{20}$$

According to the last two equations the derivatives of the rotation matrices with respect to the angles α_x, α_y, α_z can be written as products of the rotation matrices and the matrix representations of the angular momentum operators. The latter are in the spherical tensor formalism sparse matrices, which up to order L in the angular momentum expansion have at most $2 \times L^2$ nonvanishing elements.

$$D^{(l),\alpha_\nu}_{m'm}(\hat{R}_\Omega^{-1}) = \left(\frac{\partial}{\partial\alpha_\nu}D^{(l)}_{m'm}(\hat{R}_\Omega^{-1})\right)_0 = \left[\left(\frac{\partial}{\partial\alpha_\nu}\hat{R}_\Omega^{-1}(\alpha)\right)_0\right]^{(l)}_{m'm} \tag{21}$$

$$= \left[i\hat{L}_\nu\,\hat{R}_\Omega^{-1}\right]^{(l)}_{m'm} = \sum_k \left[i\hat{L}_\nu\right]^{(l)}_{m'k} D^{(l)}_{km}(\hat{R}_\Omega^{-1}). \tag{22}$$

The matrix representations of $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ in the complex and in the real spherical tensor formalism are given in Table 1.

In addition to the derivatives of the rotation matrices with respect to the angles α we also need the derivatives of the functions $G^n_{l_a l_b j}$ with respect to the intermolecular distance $G^{n,R}_{l_a l_b j}$. If these ingredients are available, the first derivatives of the pair potential in Eq. (9) can be calculated as follows:

Table 1
Matrix representations for the operators $[i\widehat{L}_x]$, $[i\widehat{L}_y]$ and $[i\widehat{L}_z]$ for the complex and real spherical representations. All nonvanishing matrix elements are given. The numerical coefficients C^+ and C^- are defined as $C^+(l,m) = \sqrt{l(l+1) - m(m+1)}$ and $C^-(l,m) = \sqrt{l(l+1) - m(m-1)}$

	$[i\widehat{L}_x]$	$[i\widehat{L}_y]$	$[i\widehat{L}_z]$
complex spherical representation			
m, m	$[i\widehat{L}_x]^{(l)}_{m,m-1} = +\frac{1}{2}iC^-(l,0)$	$[i\widehat{L}_y]^{(l)}_{m,m-1} = -\frac{1}{2}C^-(l,0)$	$[i\widehat{L}_z]^{(l)}_{m,m} = im$
	$[i\widehat{L}_x]^{(l)}_{m,m+1} = +\frac{1}{2}iC^+(l,0)$	$[i\widehat{L}_y]^{(l)}_{m,m+1} = +\frac{1}{2}C^+(l,0)$	
real spherical representation			
$0, \kappa$	$[i\widehat{L}_x]^{(l)}_{0,1s} = +\frac{1}{\sqrt{2}}C^+(l,0)$	$[i\widehat{L}_y]^{(l)}_{0,1c} = -\frac{1}{\sqrt{2}}C^+(l,0)$	
$1c, \kappa$		$[i\widehat{L}_y]^{(l)}_{1c,0} = +\frac{1}{\sqrt{2}}C^-(l,1)$	$[i\widehat{L}_z]^{(l)}_{1c,1s} = -1$
	$[i\widehat{L}_x]^{(l)}_{1c,2s} = +\frac{1}{2}C^+(l,1)$	$[i\widehat{L}_y]^{(l)}_{1c,2c} = -\frac{1}{2}C^+(l,1)$	
$1s, \kappa$	$[i\widehat{L}_x]^{(l)}_{1s,0} = -\frac{1}{\sqrt{2}}C^-(l,1)$		$[i\widehat{L}_z]^{(l)}_{1s,1c} = +1$
	$[i\widehat{L}_x]^{(l)}_{1s,2c} = -\frac{1}{2}C^+(l,1)$	$[i\widehat{L}_y]^{(l)}_{1s,2s} = -\frac{1}{2}C^+(l,1)$	
kc, κ	$[i\widehat{L}_x]^{(l)}_{kc,(k-1)s} = +\frac{1}{2}C^-(l,k)$	$[i\widehat{L}_y]^{(l)}_{kc,(k-1)c} = +\frac{1}{2}C^-(l,k)$	$[i\widehat{L}_z]^{(l)}_{kc,ks} = -k$
	$[i\widehat{L}_x]^{(l)}_{kc,(k+1)s} = +\frac{1}{2}C^+(l,k)$	$[i\widehat{L}_y]^{(l)}_{kc,(k+1)c} = -\frac{1}{2}C^+(l,k)$	
ks, κ	$[i\widehat{L}_x]^{(l)}_{ks,(k-1)c} = -\frac{1}{2}C^-(l,k)$	$[i\widehat{L}_y]^{(l)}_{ks,(k-1)s} = -\frac{1}{2}C^-(l,k)$	$[i\widehat{L}_z]^{(l)}_{ks,kc} = +k$
	$[i\widehat{L}_x]^{(l)}_{ks,(k+1)c} = -\frac{1}{2}C^+(l,k)$	$[i\widehat{L}_y]^{(l)}_{ks,(k+1)c} = +\frac{1}{2}C^+(l,k)$	

$$\overline{S}^{k_a k_b,\alpha_\nu^A}_{l_a l_b j} = \sum_m D^{(l_a),\alpha_\nu^A}_{m k_a}(\tilde{\Omega}_a) D^{(l_b)}_{m k_b}(\tilde{\Omega}_b) s_{l_a,l_b,j,m}, \tag{23}$$

$$\overline{S}^{k_a k_b,\alpha_\nu^B}_{l_a l_b j} = \sum_m D^{(l_a)}_{m k_a}(\tilde{\Omega}_a) D^{(l_b),\alpha_\nu^B}_{m k_b}(\tilde{\Omega}_b) s_{l_a,l_b,j,m}, \tag{24}$$

$$E^{AB,\alpha_\nu^A} = \sum_{\substack{n k_a k_b \\ l_a l_b j}} C^{k_a k_b}_{l_a l_b j n} \overline{S}^{k_a k_b,\alpha_\nu^A}_{l_a l_b j} G^n_{l_a l_b j}(R), \tag{25}$$

$$E^{AB,\alpha_\nu^B} = \sum_{\substack{n k_a k_b \\ l_a l_b j}} C^{k_a k_b}_{l_a l_b j n} \overline{S}^{k_a k_b,\alpha_\nu^B}_{l_a l_b j} G^n_{l_a l_b j}(R), \tag{26}$$

$$E^{AB,R} = \sum_{\substack{n k_a k_b \\ l_a l_b j}} C^{k_a k_b}_{l_a l_b j n} \overline{S}^{k_a k_b}_{l_a l_b j} G^{n,R}_{l_a l_b j}(R), \tag{27}$$

where the numerical factors $s_{l_a,l_b,j,m}$ are defined as

$$s_{l_a,l_b,j,m} = i^{l_a - l_b - j} \begin{pmatrix} l_a & l_b & j \\ m & m & 0 \end{pmatrix} \begin{pmatrix} l_a & l_b & j \\ 0 & 0 & 0 \end{pmatrix}^{-1}. \tag{28}$$

Because the space-fixed z-axis was chosen parallel to the intermolecular distance vector so that $\frac{1}{2}(\tilde{\psi}_a + \tilde{\psi}_b)$ became an external variable, the two derivatives with respect to rotations of the molecules through this axis, $E^{\alpha_z^A}_{AB}$ and $E^{\alpha_z^A}_{AB}$, are related by the equation:

$$E^{\alpha_z^B}_{AB} = -E^{\alpha_z^A}_{AB}. \tag{29}$$

Thus the proposed approach leads to the minimal number of 6 contributions to the first derivatives, in contrast to the 16 contributions that have to be calculated in the method developed in Refs. [9,10].

If the $\bar{S}$ functions and their derivatives are calculated via recurrence relations, the energy and the first derivatives of this general ansatz for a pair potential can be evaluated up to order L in the angular momentum expansion and up to order n in the expansion for the distance dependence with computational expenditure of $\mathcal{O}(n \times L^5)$, but for many of the contributions to Van der Waals potentials the coefficients $C_{l_a l_b jn}^{k_a k_b}$ can be factorized and/or one or both of the indices j and n drop out and more efficient implementations can be obtained using specialized expressions.

For example, the electrostatic interaction energy and its derivatives can be computed with only $\mathcal{O}(L^3)$ operations. For this interaction the distance dependence is described by the multipole interaction tensors $t_m^{(l_a,l_b)}(R)$. The derivatives of these tensors are obtained as:

$$\frac{\partial}{\partial R} t_m^{(l_a,l_b)} = R^{-l_a-l_b-2} \frac{(-1)^{l_b}}{4\pi\epsilon_0} (-l_a - l_b - 1) \sqrt{\binom{l_a+l_b}{l_a+m}\binom{l_a+l_b}{l_a-m}} \tag{30}$$

$$= -\sqrt{(l_a+1+m)(l_a+1-m)}\, t_m^{(l_a+1,l_b)}(R). \tag{31}$$

The energy and first derivatives for the electrostatic interaction can then be evaluated by the following algorithm:

$$\widetilde{Q}_{l\kappa}^{A} = \sum_{\kappa'} {}^{r}D_{\kappa\kappa'}^{(l)}(\widetilde{\Omega}_A) Q_{l\kappa'}^{A}, \qquad \widetilde{Q}_{l\kappa}^{B} = \sum_{\kappa'} {}^{r}D_{\kappa\kappa'}^{(l)}(\widetilde{\Omega}_B) Q_{l\kappa'}^{B},$$

$$\widetilde{Q}_{l\kappa}^{A,\alpha_\nu^A} = \sum_{\kappa'} \left[i\widehat{L}_\nu\right]_{\kappa\kappa'} \widetilde{Q}_{l\kappa'}^{A}, \qquad \widetilde{Q}_{l\kappa}^{B,\alpha_\nu^B} = \sum_{\kappa'} \left[i\widehat{L}_\nu\right]_{\kappa\kappa'} \widetilde{Q}_{l\kappa'}^{B},$$

$$\widetilde{V}_{l\kappa}^{AB} = \sum_{l'} t_\kappa^{(l,l')} \widetilde{Q}_{l'\kappa}^{B}, \qquad \widetilde{V}_{l\kappa}^{BA} = \sum_{l'} t_\kappa^{(l,l')} \widetilde{Q}_{l'\kappa}^{A},$$

$$\widetilde{V}_{l\kappa}^{AB,R} = -\sqrt{(l+1+|\kappa|)(l+1-|\kappa|)}\, \widetilde{V}_{l+1,\kappa}^{AB},$$

$$E_{AB} = \sum_{l\kappa} \widetilde{Q}_{l\kappa}^{A} \widetilde{V}_{l\kappa}^{AB}, \qquad E_{AB}^{\alpha_\nu^A} = \sum_{l\kappa} \widetilde{Q}_{l\kappa}^{A,\alpha_\nu^A} \widetilde{V}_{l\kappa}^{AB},$$

$$E_{AB}^{R} = \sum_{l\kappa} \widetilde{Q}_{l\kappa}^{A} \widetilde{V}_{l\kappa}^{AB,R}, \qquad E_{AB}^{\alpha_\nu^B} = \sum_{l\kappa} \widetilde{Q}_{l\kappa}^{B,\alpha_\nu^B} \widetilde{V}_{l\kappa}^{BA}.$$

After calculation of the rotation matrices ${}^{r}D(\widetilde{\Omega}_A)$ and ${}^{r}D(\widetilde{\Omega}_B)$ and the intermediates for the energy t, $\widetilde{Q}^A$, $\widetilde{Q}^B$, $\widetilde{V}^{AB}$, only one additional intermediate with computational costs of $\mathcal{O}(L^3)$, the vector $\widetilde{V}^{BA}$, has to be evaluated for the calculation of first derivatives. For all other steps the expenditures scale as $\mathcal{O}(L^2)$.

From the derivatives $E_{AB}^{\alpha_\nu^A}$, $E_{AB}^{\alpha_\nu^B}$ and E_{AB}^{R} the components of the forces and torques on the molecules A and B are obtained as:

$$\widetilde{F}_x^A = -\left(E_{AB}^{\alpha_y^A} + E_{AB}^{\alpha_y^B}\right)/R, \qquad \widetilde{F}_y^A = \left(E_{AB}^{\alpha_x^A} + E_{AB}^{\alpha_x^B}\right)/R, \qquad \widetilde{F}_z^A = E_{AB}^{R} \tag{32}$$

and

$$\widetilde{T}_\nu^A = -E_{AB}^{\alpha_\nu^A}, \qquad \widetilde{T}_\nu^B = -E_{AB}^{\alpha_\nu^B}. \tag{33}$$

The force on molecule B is, as required by Newton's law of action and reaction, the negative of the force on molecule A:

$$\widetilde{F}^B = -\widetilde{F}^A.$$

The forces and torques obtained in the quasi-internal coordinate system can now be transformed to any suitable coordinate system, e.g. the space-fixed reference system or to the molecule-fixed systems by multiplication with the respective Cartesian 3×3 rotation matrix.

4. Calculation of second and higher derivatives

With the approach devised in Section 3 the calculation of second and higher derivatives is now almost straightforward, but one has to take care of the subtle details caused by the fact that rotation operations, in general, do not commute. Thus, for the respective combinations of variables the second derivatives of the energy or of intermediates cannot be calculated by simply taking the derivative of the result obtained for a first derivative, for example

$$\left(\frac{\partial}{\partial\alpha_x^A\partial\alpha_y^A}E(\tilde{\Omega}^A,\tilde{\Omega}^B,R)\right)_0 \neq \left(\frac{\partial}{\partial\alpha_x^A}E^{\alpha_y^A}(\tilde{\Omega}^A,\tilde{\Omega}^B,R)\right)_0 . \tag{34}$$

In the quasi-internal coordinate system the rotations of molecule A commute with the rotations of molecule B as well as with the stretching of the intermolecular distance. Nonvanishing commutators arise only between rotations of the same molecule about two different axes. This affects only the mixed derivatives of the rotation matrices. They are obtained as follows:

$$\begin{aligned}\hat{R}_\Omega^{-1}(\alpha) &= \exp\left(i\alpha_x\hat{L}_{x\Omega}+i\alpha_y\hat{L}_{y\Omega}+i\alpha_z\hat{L}_{z\Omega}\right)\hat{R}_\Omega^{-1}\\ &= \sum_{n=0}^{\infty}\frac{1}{n}\left(i\alpha_x\hat{L}_{x\Omega}+i\alpha_y\hat{L}_{y\Omega}+i\alpha_z\hat{L}_{z\Omega}\right)^n\hat{R}_\Omega^{-1},\end{aligned} \tag{35}$$

$$\left(\frac{\partial}{\partial\alpha_\nu\partial\alpha_\mu}\hat{R}_\Omega^{-1}(\alpha)\right)_0 = -\tfrac{1}{2}(\hat{L}_{\nu\Omega}\hat{L}_{\mu\Omega}+\hat{L}_{\mu\Omega}\hat{L}_{\nu\Omega})\hat{R}_\Omega^{-1}, \tag{36}$$

$$\begin{aligned}D_{m'm}^{(l),\alpha_\nu\alpha_\mu}(\hat{R}_\Omega^{-1}) &= \left(\frac{\partial}{\partial\alpha_\nu\partial\alpha_\mu}D_{m'm}^{(l)}(\hat{R}_\Omega^{-1})\right)_0 = \left[\left(\frac{\partial}{\partial\alpha_\nu\partial\alpha_\mu}\hat{R}_\Omega^{-1}(\alpha)\right)_0\right]_{m'm}^{(l)}\\ &= \tfrac{1}{2}\sum_{k'k}\left(\left[i\hat{L}_\nu\right]_{m'k'}^{(l)}\left[i\hat{L}_\mu\right]_{k'k}^{(l)}+\left[i\hat{L}_\mu\right]_{m'k'}^{(l)}\left[i\hat{L}_\nu\right]_{k'k}^{(l)}\right)D_{km}^{(l)}(\hat{R}_\Omega^{-1})\\ &= \tfrac{1}{2}\sum_{k}\left\{\left[i\hat{L}_\nu\right]_{m'k}^{(l)}D_{km}^{(l),\alpha_\mu}(\hat{R}_\Omega^{-1})+\left[i\hat{L}_\mu\right]_{m'k}^{(l)}D_{km}^{(l),\alpha_\nu}(\hat{R}_\Omega^{-1})\right\}.\end{aligned} \tag{37}$$

The last equation can be generalized to a recurrence relation for arbitrary higher mixed derivatives of the rotation matrices:

$$D_{m'm}^{(l),\alpha_x^r\alpha_y^s\alpha_z^t} = \frac{1}{r+s+t}\sum_k\left\{r\left[i\hat{L}_x\right]_{m'k}^{(l)}D_{km}^{(l),\alpha_x^{r-1}\alpha_y^s\alpha_z^t}+s\left[i\hat{L}_y\right]_{m'k}^{(l)}D_{km}^{(l),\alpha_x^r\alpha_y^{s-1}\alpha_z^t}+t\left[i\hat{L}_z\right]_{m'k}^{(l)}D_{km}^{(l),\alpha_x^r\alpha_y^s\alpha_z^{t-1}}\right\}. \tag{38}$$

Based on Eq. (37), the algorithm for the electrostatic energy and its first derivatives proposed in Section 3 can be extended for the second derivatives as follows:

$$\tilde{Q}_{l\kappa}^{A,\alpha_\nu^A\alpha_\mu^A} = \tfrac{1}{2}\sum_{\kappa'}\left\{\left[i\hat{L}_\nu\right]_{\kappa\kappa'}\tilde{Q}_{l\kappa'}^{A,\alpha_\mu^A}+\left[i\hat{L}_\mu\right]_{\kappa\kappa'}\tilde{Q}_{l\kappa'}^{A,\alpha_\nu^A}\right\},$$

$$\widetilde{Q}_{l\kappa}^{B,\alpha_\nu^B\alpha_\mu^B} = \tfrac{1}{2}\sum_{\kappa'}\left\{\left[i\widehat{L}_\nu\right]_{\kappa\kappa'}\widetilde{Q}_{l\kappa'}^{B,\alpha_\mu^B} + \left[i\widehat{L}_\mu\right]_{\kappa\kappa'}\widetilde{Q}_{l\kappa'}^{B,\alpha_\nu^B}\right\},$$

$$\widetilde{V}_{l\kappa}^{AB,R^2} = -\sqrt{(l+1+|\kappa|)(l+1-|\kappa|)}\;\widetilde{V}_{l+1,\kappa}^{AB,R},$$

$$\widetilde{V}_{l\kappa}^{BA,R} = -\sqrt{(l+1+|\kappa|)(l+1-|\kappa|)}\;\widetilde{V}_{l+1,\kappa}^{BA},$$

$$\widetilde{V}_{l\kappa}^{AB,\alpha_\nu^B} = \sum_{l'} {}^{r}t_\kappa^{(l,l')}\;\widetilde{Q}_{l',\kappa}^{B,\alpha_\nu^B},$$

$$E_{AB}^{\alpha_\nu^A,\alpha_\mu^A} = \sum_{l\kappa}\widetilde{Q}_{l\kappa}^{A,\alpha_\nu^A,\alpha_\mu^A}\widetilde{V}_{l\kappa}^{AB}, \qquad E_{AB}^{\alpha_\nu^B,\alpha_\mu^B} = \sum_{l\kappa}\widetilde{Q}_{l\kappa}^{B,\alpha_\nu^B,\alpha_\mu^B}\widetilde{V}_{l\kappa}^{BA},$$

$$E_{AB}^{\alpha_\nu^A,R} = \sum_{l\kappa}\widetilde{Q}_{l\kappa}^{A,\alpha_\nu^A}\widetilde{V}_{l\kappa}^{AB,R}, \qquad E_{AB}^{\alpha_\nu^B,R} = \sum_{l\kappa}\widetilde{Q}_{l\kappa}^{B,\alpha_\nu^B}\widetilde{V}_{l\kappa}^{BA,R},$$

$$E_{AB}^{\alpha_\nu^A,\alpha_\mu^B} = \sum_{l\kappa}\widetilde{Q}_{l\kappa}^{A,\alpha_\nu^A}\;\widetilde{V}_{l\kappa}^{AB,\alpha_\mu^B}, \qquad E_{AB}^{R^2} = \sum_{l\kappa}\widetilde{Q}_{l\kappa}^{A}\widetilde{V}_{l\kappa}^{AB,R^2}.$$

There are again for symmetry reasons some relations between the derivatives:

$$E_{AB}^{\alpha_x^A,\alpha_z^A} = -E_{AB}^{\alpha_x^A,\alpha_z^B} - \tfrac{1}{2}E^{\alpha_y^A}, \qquad E_{AB}^{\alpha_x^B,\alpha_z^B} = -E_{AB}^{\alpha_x^B,\alpha_z^A} - \tfrac{1}{2}E^{\alpha_y^B},$$

$$E_{AB}^{\alpha_y^A,\alpha_z^A} = -E_{AB}^{\alpha_y^A,\alpha_z^B} + \tfrac{1}{2}E^{\alpha_x^A}, \qquad E_{AB}^{\alpha_y^B,\alpha_z^B} = -E_{AB}^{\alpha_y^B,\alpha_z^A} + \tfrac{1}{2}E^{\alpha_x^B},$$

$$E_{AB}^{\alpha_z^A,\alpha_z^A} = -E_{AB}^{\alpha_z^A,\alpha_z^B}, \qquad E_{AB}^{\alpha_z^B,\alpha_z^B} = -E_{AB}^{\alpha_z^B,\alpha_z^A},$$

$$E_{AB}^{R,\alpha_z^A} = -E_{AB}^{R,\alpha_z^B}.$$

Thus only $6 \times 7/2 = 21$ independent second derivatives have to be calculated. As for the first derivatives, the operation count scales for most of the steps as $\mathcal{O}(L^2)$, only the calculation of $\widetilde{V}^{AB,\alpha_\nu^B}$ scales as $\mathcal{O}(L^3)$.

Higher derivatives of the electrostatic energy are rarely needed and we will therefore not give any explicit formulae for their implementation, but, in principle, they can be made available for arbitrarily high orders through recurrence relations derived from Eq. (38). Analogous algorithms can be derived for the gradients and the Hessians of the second-order induction and dispersion energies. Using for the derivatives similar intermediates as were proposed in Ref. [8] for the respective energies, the gradients and Hessians can be implemented at small extra cost to the energy calculations.

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