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AN ANALYTICAL COMPUTATION OF CHRISTOFFEL SYMBOLS FOR REACTION COORDINATE AND TRAJECTORY TREATMENTS UNDER INTERNAL COORDINATES

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Abstract

We examine the Hessian matrix of the potential energy under internal coordinates. We report all Christoffel symbols which exist for molecules if we use the known coordinates such as bond distances, bond angles, torsion angles, and out-of-plane angles. We use as an example triatomic HCN in an extended geometry.

1. Introduction

Reaction coordinates, or considerations of molecule trajectories in a chemical rearrangement, are based on the assumption that the potential energy V is a function of the relative position of the nuclei. Thus, an important theoretical tool is the computation of the potential energy surface (PES), or of some lower-dimensional sections of it, where the atomic nuclei move and we observe the change in their potential energy if we trace a corresponding trajectory on the PES. In general, variations of bond lengths, valence angles and dihedral angles within the molecule represent a convenient set of coordinates. A suitable definition of a continuous line in these coordinates representing a "reaction coordinate" (whatever this means), has stood in the center of the scientific debate for many years (cf. [1]). It seems necessary to use fundamental ideas of differential geometry to reach a definition which is independent of the choice of coordinate system. In the case of the intrinsic reaction coordinate (IRC) [2], a path function $\boldsymbol{q} = \boldsymbol{q}(t)$ traces a path in configuration space, which is the steepest descent path on the PES, connecting a saddle point with a minimum of the PES. We obtain an independent definition of an IRC by use of the contravariant metric coefficients g^{kl} of the curvilinear coordinates q^i, in comparison with the Cartesian δ^{kl}, by using a simple gradient system of ordinary differential equations for the path

$$\mathrm{d}q^i/\mathrm{d}t = -g^{ij}(\partial V/\partial q^j), \tag{1}$$

where $g = \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^{\mathrm{T}}$. (The sum goes over j from 1 to n in the Einstein sum convention.) **B** is the Wilson **B** matrix and **M** is the diagonal mass matrix. Unfortunately, the simple gradient ansatz of a steepest descent [3–5] is usable only as a global concept; it is not usable as a local criterion for a path on the PES. If we are interested in a local property, such as a valley floor characterization at any point on a so-called minimum energy path (cf. [6]), then we have to use second derivatives of the PES, which comprise the Hessian matrix [7–11]. We trace a path on which the eigenvector of the Hessian and the gradient vector are parallel, using the ansatz of a gradient extremal. To be independent of a coordinate system necessitates that in the derivation of the Hessian we use the covariant vector $(\partial V/\partial q^i)$. In a curvilinear coordinator system $(q^i)_{i=1,\dots,n}$, this results in (cf. [8])

$$H_{ij} = V_{;q^iq^j} = \partial^2 V/\partial q^i \partial q^j - \Gamma_{ij}^k(\partial V/\partial q^k), \tag{2}$$

where the Christoffel symbols of second kind Γ_{ij}^k emerge, which depend directly on the metric coefficients

$$\Gamma_{ij}^k = \tfrac{1}{2}\, g^{kl}(\partial g_{jl}/\partial q^i + \partial g_{il}/\partial q^j - \partial g_{ij}/\partial q^l). \tag{3}$$

At a nonequilibrium point of the PES, we can compute generalized normal vibrations of the molecule [12,13] by diagonalizing the Hessian matrix as defined in eq. (2). We obtain a matrix of force constants. Nota bene, the matrix $(\partial^2 V/\partial q^i \partial q^j)$, which gives the "basic force constants", is not a tensor [14]; it depends on the choice of coordinate system. The generalized normal vibrations may be used in an extension of the so-called reaction path Hamiltonian [15,16] in curvilinear coordinates.

In a more dynamic way, if we treat classical equations of motion of the atomic nuclei in the molecule, then we have to use the Lagrange ansatz in the mass weighted form of eq. (1) (cf. [17,18]),

$$-\mathrm{d}^2 q^k/\mathrm{d}t^2 = \Gamma_{ij}^k(\mathrm{d}q^i/\mathrm{d}t)(\mathrm{d}q^j/\mathrm{d}t) + g^{kl}(\partial V/\partial q^l). \tag{4}$$

Thus, we have to deal with the Christoffel symbols as well. In eq. (4) we observe, in the case of constant energy V, the condition for an unperturbed kinematically possible motion of the system point, because the term on the r.h.s. becomes zero. The trajectory becomes a geodesic curve of least curvature due to the fact that eq. (4) is cast in the form

$$-\mathrm{d}^2 q^k/\mathrm{d}t^2 = \Gamma_{ij}^k(\mathrm{d}q^i/\mathrm{d}t)(\mathrm{d}q^j/\mathrm{d}t) \tag{5}$$

(cf. [19]; this reference deals with such problems in a reaction problem).

The apparent complication which emerges with the sum of the Christoffel symbols serves as a corrigendum against the influence of the curvilinear coordinate system which, in reality, should not have an influence on the motion. We can imagine a small person with a hammer riding on the curve $q(t)$ and, as the curve tries to pop out of its straight path, he or she continuously pounds it back in because of the fundamental law: every free system persists in its state of rest or uniform motion in a straight path.

All that is necessary now is to evaluate an algorithm to compute the Γ_{ij}^k in those coordinate systems which are generally used for small and medium-sized molecules.

2. Analytical computation of Christoffel symbols of second kind

The Christoffel symbols of second kind, eq. (3), are computed by

$$\Gamma_{ij}^k = -\sum_v \sum_w g_{il}(\partial q^l/\partial x^v)(\partial^2 q^k/\partial x^v \partial x^w)(\partial q^r/\partial x^w) g_{rj}, \tag{6}$$

where q^i denote the internal and x^v the Cartesian coordinates of the molecule. g_{ij} are the elements of the covariant metric tensor given by

$$\delta_i^j = \sum_v g_{ik}(\partial q^k/\partial x^v)(\partial q^j/\partial x^v). \tag{7}$$

The task is the analytical computation of the first and second derivations of the internal coordinates with respect to Cartesian ones. The internal coordinates are divided into bond length, bond angle, torsion angle and out-of-plane angle.

A procedure is well known [20] which realizes the task in a non-analytical ansatz, using the expansion of curvilinear coordinates and potential energy. We note that we are interested also in points far away from equilibrium geometries; this is a step beyond ref. [20].

The computation of the derivations has been carried out according to the following algorithm. Firstly, derivations are computed in dependence on Cartesian coordinates by use of the formula manipulation package REDUCE [21]. Secondly, the Cartesian coordinates are substituted by internal coordinates which lie in a selected position in space.

The particular space position $\bar{x}$ of every one of the atoms which define an internal coordinate is also represented independently of internal coordinates given by

$$\bar{x} = \mathbf{T}^{\mathrm{T}}(x + v). \tag{8}$$

Matrix $\mathbf{T}$ is the result of the multiplication of the matrices of rotation $\mathbf{D}_x$, $\mathbf{D}_y$ and $\mathbf{D}_z$. The elements of the matrix $\mathbf{T}$ are given by

$$T_{11} = \cos(\alpha)\cos(\beta), \tag{9}$$

$$T_{12} = \sin(\alpha)\cos(\gamma) + \cos(\alpha)\sin(\beta)\sin(\gamma), \tag{10}$$

$$T_{19} = \sin(\alpha)\sin(\gamma) - \cos(\alpha)\sin(\beta)\cos(\gamma), \tag{11}$$

$$T_{21} = -\sin(\alpha)\cos(\beta), \tag{12}$$

$$T_{22} = \cos(\alpha)\cos(\gamma) - \sin(\alpha)\sin(\beta)\sin(\gamma), \tag{13}$$

$$T_{23} = \cos(\alpha)\sin(\gamma) + \sin(\alpha)\sin(\beta)\cos(\gamma), \tag{14}$$

$$T_{31} = \sin(\beta), \tag{15}$$

$$T_{32} = -\cos(\beta)\sin(\gamma), \tag{16}$$

$$T_{33} = \cos(\beta)\cos(\gamma). \tag{17}$$

Angles α, β, and γ are defined in the appendix. Vector v is the vector of translation of the atoms which define an internal coordinate. v is given by

$$v^{\mathrm{T}} = (-x^{3b-2} - x^{3b-1} - x^{3b}), \tag{18}$$

and b is the number of an atom. For torsion angle $\vartheta(r_a\ r_b, r_c, r_d)$, for example, the following terms result:

$$\bar{x}^{3a-2} = -r_{ab}\cos(\varphi), \tag{19}$$

$$\bar{x}^{3a-1} = r_{ab}\sin(\varphi)\cos(\vartheta), \tag{20}$$

$$\bar{x}^{3a} = r_{ab}\sin(\varphi)\sin(\vartheta), \tag{21}$$

$$\bar{x}^{3c-2} = -r_{bc}, \tag{22}$$

$$\bar{x}^{3d-2} = -r_{bd}\cos(\delta), \tag{23}$$

$$\bar{x}^{3d-1} = r_{bd}\sin(\delta), \tag{24}$$

$$\bar{x}^{3b-2} = \bar{x}^{3b-1} = \bar{x}^{3b} = \bar{x}^{3c-1} = \bar{x}^{3c} = \bar{x}^{3d} = 0. \tag{25}$$

The angles φ and δ are given by

$$\varphi = \arccos\big((\boldsymbol{r}_a - \boldsymbol{r}_b)(\boldsymbol{r}_c - \boldsymbol{r}_b)/(r_{ab}r_{bc})\big), \tag{26}$$

$$\delta = \arccos\big((\boldsymbol{r}_c - \boldsymbol{r}_b)(\boldsymbol{r}_d - \boldsymbol{r}_b)/(r_{bc}r_{bd})\big), \tag{27}$$

where $r_{ab} = |\boldsymbol{r}_a - \boldsymbol{r}_b|$.

Matrix **T** transforms from a particular space position into an arbitrary one.

For all internal coordinates q^i, the first derivations in eq. (6) are given by

$$\partial q^i/\partial x^v = \sum_{r=1}^{3} T_{v-t\ r} E_{t+r}^{\text{type of } q^i} \tag{28}$$

and the second ones are given by

$$\partial^2 q^i/\partial x^v \partial x^w = \sum_{r=1}^{3} \sum_{s=1}^{3} T_{v-t\ r} T_{w-u\ s} F_{t+r\ u+s}^{\text{type of } q^i}, \tag{29}$$

where

$$t = 3[(v-1)/3], \quad u = 3[(w-1)/3], \tag{30}$$

and the angular bracket $[z]$ means the entire part of number z. Vector $\boldsymbol{E}$ and matrix **F** are given by

$$E_v^{\text{type of } q^i} = \partial q^i/\partial \bar{x}^v \tag{31}$$

$$F_{vw}^{\text{type of } q^i} = \partial^2 q^i/\partial \bar{x}^v \partial \bar{x}^w \tag{32}$$

All elements of vector $\boldsymbol{E}$ and matrix **F** different from zero are summarized in the appendix for all types of internal coordinates, as well as the formulas for the computation of the angles α, β, and γ. If the reader would like to use the given expressions for dynamical treatments, this can be done by a simple mass-weighting extension of eq. (6).

$$\Gamma_{ij}^{k} = -g_{il}(\partial q^l/\partial x^t) m^{tu} (\partial^2 q^k/\partial x^u \partial x^v) m^{vw} (\partial q^r/\partial x^w) g_{rj}. \tag{33}$$

m^{tu} is the inverse mass matrix g_{il} and g_{rj}, see eq. (1). Instructive examples are given in ref. [22] in the case of tri- and tetra-atomic molecules. We have a program for the compilation of the Christoffel symbols of second kind, on diskette written in FORTRAN 77, which is available on request.

3. Example

There are 4 internal coordinates and 64 Christoffel symbols of second kind for the molecule HCN [6]. The internal coordinates are defined by

$$q^1 = r_{\text{CH}}, \qquad q^2 = r_{\text{CN}}, \qquad q^3 = \eta_{\text{HCN}}, \qquad q^4 = \kappa_{\text{HCN}},$$

where a point of the dissociation path to H+CN with maximal value of the gradient is [23]:

$$r_{CH} = 170.0 \text{ pm}, \quad r_{CN} = 116.0 \text{ pm}, \quad \eta_{HCN} = \pi, \quad \kappa_{HCN} = \pi.$$

This point is extended from the equilibrium geometry. Only 12 Christoffel symbols of second kind are different from zero, and are given by:

$$\Gamma^3_{13} = \Gamma^3_{31} = \Gamma^4_{14} = \Gamma^4_{41} = 2.209436 \text{ nm}^{-1},$$

$$\Gamma^3_{23} = \Gamma^3_{32} = \Gamma^4_{24} = \Gamma^4_{42} = 5.382723 \text{ nm}^{-1},$$

$$\Gamma^1_{33} = \Gamma^1_{44} = -23.983335 \text{ pm rad}^{-1},$$

$$\Gamma^2_{33} = \Gamma^2_{44} = -45.224948 \text{ pm rad}^{-2}.$$

Appendix

Bond length r

$r(\boldsymbol{r}_a, \boldsymbol{r}_b) = r_{ab}$

$u_1 = y^a - y^b, \quad v_1 = x^a - x^b$

$\sin(\alpha) = \sin(\arctan(u_1/v_1))$		$v_1 < 0$
$\sin(\alpha) = 1$	$u_1 < 0,$	$v_1 = 0$
$\sin(\alpha) = 0$	$u_1 = 0,$	$v_1 = 0$
$\sin(\alpha) = -1$	$u_1 > 0,$	$v_1 = 0$
$\sin(\alpha) = -\sin(\arctan(u_1/v_1))$		$v_1 > 0$
$\cos(\alpha) = -\cos(\arctan(u_1/v_1))$		$v_1 < 0$
$\cos(\alpha) = 0$	$u_1 \neq 0,$	$v_1 = 0$
$\cos(\alpha) = 1$	$u_1 = 0,$	$v_1 = 0$
$\cos(\alpha) = \cos(\arctan(u_1/v_1))$		$v_1 > 0$

$u_2 = z^a - z^b, \quad v_2 = \cos(\alpha)(x^a - x^b) - \sin(\alpha)(y^a - y^b)$

$\sin(\beta) = \sin(\arctan(u_2/v_2))$		$v_2 > 0$
$\sin(\beta) = -1$	$u_2 < 0,$	$v_2 = 0$
$\sin(\beta) = 1$	$u_2 > 0,$	$v_2 = 0$
$\cos(\beta) = \cos(\arctan(u_2/v_2))$		$v_2 > 0$
$\cos(\beta) = 0$		$v_2 = 0$

$\sin(\gamma) = 0$

$\cos(\gamma) = 1$

$E_{3a-2} = 1$

$E_{3b-2} = -1$

$F_{3a-1\,3a-1} = 1/r$

$F_{3a-1\,3b-1} = -1/r$

$F_{3a\,3a} = 1/r$

$F_{3a\,3b} = -1/r$
$F_{3b-1\,3b-1} = 1/r$
$F_{3b\,3b} = 1/r$

First linear bond angle η

$\eta(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c) = \arccos((\boldsymbol{r}_a - \boldsymbol{r}_b)(\boldsymbol{r}_c - \boldsymbol{r}_b)/(r_{ab}\, r_{bc})), \quad \eta = \pi$
$u_1 = y^c - y^b, \quad v_1 = x^c - x^b$
$\sin(\alpha) = -\sin(\arctan(u_1/v_1)) \qquad v_1 < 0$
$\sin(\alpha) = -1 \qquad u_1 < 0, \quad v_1 = 0$
$\sin(\alpha) = 0 \qquad u_1 = 0, \quad v_1 = 0$
$\sin(\alpha) = 1 \qquad u_1 > 0, \quad v_1 = 0$
$\sin(\alpha) = \sin(\arctan(u_1/v_1)) \qquad v_1 > 0$
$\cos(\alpha) = \cos(\arctan(u_1/v_1)) \qquad v_1 < 0$
$\cos(\alpha) = 0 \qquad u_1 \neq 0, \quad v_1 = 0$
$\cos(\alpha) = 1 \qquad u_1 = 0, \quad v_1 = 0$
$\cos(\alpha) = -\cos(\arctan(u_1/v_1)) \qquad v_1 > 0$
$u_2 = z^c - z^b, \quad v_2 = \cos(\alpha)(x^c - x^b) - \sin(\alpha)(y^c - y^b)$
$\sin(\beta) = \sin(\arctan(u_2/v_2)) \qquad v_2 < 0$
$\sin(\beta) = 1 \qquad u_2 < 0, \quad v_2 = 0$
$\sin(\beta) = -1 \qquad u_2 > 0, \quad v_2 = 0$
$\cos(\beta) = \cos(\arctan(u_2/v_2)) \qquad v_2 < 0$
$\cos(\beta) = 0 \qquad v_2 = 0$
$\sin(\gamma) = 0$
$\cos(\gamma) = 1$
$E_{3a-1} = -1/r_{ab}$
$E_{3b-1} = (r_{ab} + r_{bc})/(r_{ab}\, r_{bc})$
$E_{3c-1} = -1/r_{bc}$
$F_{3a-2\,3a-1} = 1/r_{ab}^2$
$F_{3a-2\,3b-1} = -1/r_{ab}^2$
$F_{3a-1\,3b-2} = -1/r_{ab}^2$
$F_{3b-2\,3b-1} = (r_{bc}^2 - r_{ab}^2)/(r_{ab}^2\, r_{bc}^2)$
$F_{3b-2\,3c-1} = 1/r_{bc}^2$
$F_{3b-1\,3c-2} = 1/r_{bc}^2$
$F_{3c-2\,3c-1} = -1/r_{bc}^2$

Second linear bond angle κ

$\kappa(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c) = \arccos((\boldsymbol{r}_a - \boldsymbol{r}_b)(\boldsymbol{r}_c - \boldsymbol{r}_b)/(r_{ab}\, r_{bc})), \quad \kappa = \pi$
$u_1 = y^c - y^b, \quad v_1 = x^c - x^b$
$\sin(\alpha) = -\sin(\arctan(u_1/v_1)) \qquad v_1 < 0$

$$
\begin{array}{lll}
\sin(\alpha) = -1 & u_1 < 0, & v_1 = 0 \\
\sin(\alpha) = 0 & u_1 = 0, & v_1 = 0 \\
\sin(\alpha) = 1 & u_1 > 0, & v_1 = 0 \\
\sin(\alpha) = \sin(\arctan(u_1/v_1)) & & v_1 > 0 \\
\cos(\alpha) = \cos(\arctan(u_1/v_1)) & & v_1 < 0 \\
\cos(\alpha) = 0 & u_1 \neq 0, & v_1 = 0 \\
\cos(\alpha) = 1 & u_1 = 0, & v_1 = 0 \\
\cos(\alpha) = -\cos(\arctan(u_1/v_1)) & & v_1 > 0
\end{array}
$$

$$u_2 = z^c - z^b, \; v_2 = \cos(\alpha)(x^c - x^b) - \sin(\alpha)(y^c - y^b)$$

$$
\begin{array}{lll}
\sin(\beta) = \sin(\arctan(u_2/v_2)) & & v_2 < 0 \\
\sin(\beta) = 1 & u_2 < 0, & v_2 = 0 \\
\sin(\beta) = -1 & u_2 > 0, & v_2 = 0 \\
\cos(\beta) = \cos/\arctan(u_2/v_2)) & & v_2 < 0 \\
\cos(\beta) = 0 & & v_2 = 0 \\
\sin(\gamma) = 0 & & \\
\cos(\gamma) = 1 & &
\end{array}
$$

$$E_{3a} = -1/r_{ab}$$
$$E_{3b} = (r_{ab} + r_{bc})/(r_{ab}\, r_{bc})$$
$$E_{3c} = -1/r_{bc}$$
$$F_{3a-2\,3a} = 1/r_{ab}^2$$
$$F_{3a-2\,3b} = -1/r_{ab}^2$$
$$F_{3a\,3b-2} = -1/r_{ab}^2$$
$$F_{3b-2\,3b} = (r_{bc}^2 - r_{ab}^2)/(r_{ab}^2\, r_{bc}^2)$$
$$F_{3b-2\,3c} = 1/r_{bc}^2$$
$$F_{3b\,3c-2} = 1/r_{bc}^2$$
$$F_{3c-2\,3c} = -1/r_{bc}^2$$

Bond angle φ

$$\varphi(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c) = \arccos((\boldsymbol{r}_a - \boldsymbol{r}_b)(\boldsymbol{r}_c - \boldsymbol{r}_b)/(r_{ab}\, r_{bc})), \; 0 < \varphi < \pi$$

$$u_1 = y^c - y^b, \quad v_1 = x^c - x^b$$

$$
\begin{array}{lll}
\sin(\alpha) = -\sin(\arctan(u_1/v_1)) & & v_1 < 0 \\
\sin(\alpha) = -1 & u_1 < 0, & v_1 = 0 \\
\sin(\alpha) = 0 & u_1 = 0, & v_1 = 0 \\
\sin(\alpha) = 1 & u_1 > 0, & v_1 = 0 \\
\sin(\alpha) = \sin(\arctan(u_1/v_1)) & & v_1 > 0 \\
\cos(\alpha) = \cos(\arctan(u_1/v_1)) & & v_1 < 0 \\
\cos(\alpha) = 0 & u_1 \neq 0, & v_1 = 0 \\
\cos(\alpha) = 1 & u_1 = 0, & v_1 = 0 \\
\cos(\alpha) = -\cos(\arctan(u_1/v_1)) & & v_1 > 0
\end{array}
$$

$$
\begin{array}{llll}
u_2 & = z^c - z^b,\ v_2 = \cos(\alpha)(x^c - x^b) - \sin(\alpha)(y^c - y^b) & & \\
\sin(\beta) & = \sin(\arctan(u_2/v_2)) & & v_2 < 0 \\
\sin(\beta) & = 1 & u_2 < 0, & v_2 = 0 \\
\sin(\beta) & = -1 & u_2 > 0, & v_2 = 0 \\
\cos(\beta) & = \cos(\arctan(u_2(v_2)) & & v_2 < 0 \\
\cos(\beta) & = 0 & & v_2 = 0 \\
u_3 & = \cos(\beta)\,(z^a - z^b) - \sin(\beta)\,(\cos(\alpha)\,(x^a - x^b) - \sin(\alpha)\,(y^a - y^b)) & & \\
v_3 & = \sin(\alpha)\,(x^a - x^b) + \cos(\alpha)\,(y^a - y^b) & & \\
\sin(\gamma) & = \sin(\arctan(u_3/v_3)) & & v_3 < 0 \\
\sin(\gamma) & = -\sin(\arctan(u_3/v_3)) & & v_3 \geq 0 \\
\cos(\gamma) & = -\cos(\arctan(u_3/v_3)) & & v_3 < 0 \\
\cos(\gamma) & = \cos(\arctan(u_3/v_3)) & & v_3 \geq 0 \\
E_{3a-2} & = \sin(\varphi)/r_{ab} & & \\
E_{3a-1} & = \cos(\varphi)/r_{ab} & & \\
E_{3b-2} & = -\sin(\varphi)/r_{ab} & & \\
E_{3b-1} & = (r_{ab} - r_{bc}\cos(\varphi))/(r_{ab}\,r_{bc}) & & \\
E_{3c-1} & = -1/r_{bc} & & \\
F_{3a-2\,3a-2} & = 2\sin(\varphi)\cos(\varphi)/r_{ab}^2 & & \\
F_{3a-2\,3a-1} & = (1 - 2\sin^2(\varphi))/r_{ab}^2 & & \\
F_{3a-2\,3b-2} & = -2\sin(\varphi)\cos(\varphi)/r_{ab}^2 & & \\
F_{3a-2\,3b-1} & = (2\sin^2(\varphi) - 1)/r_{ab}^2 & & \\
F_{3a-1\,3a-1} & = -2\sin(\varphi)\cos(\varphi)/r_{ab}^2 & & \\
F_{3a-1\,3b-2} & = (2\sin^2(\varphi) - 1)/r_{ab}^2 & & \\
F_{3a-1\,3b-1} & = 2\sin(\varphi)\cos(\varphi)/r_{ab}^2 & & \\
F_{3a\,3a} & = \cos(\varphi)/(r_{ab}^2\sin(\varphi)) & & \\
F_{3a\,3b} & = (r_{ab} - r_{bc}\cos(\varphi))/(r_{ab}^2\,r_{bc}\sin(\varphi)) & & \\
F_{3a\,3c} & = -1/(r_{ab}\,r_{bc}\sin(\varphi)) & & \\
F_{3b-2\,3b-2} & = 2\sin(\varphi)\cos(\varphi)/r_{ab}^2 & & \\
F_{3b-2\,3b-1} & = (r_{bc}^2(1 - 2\sin^2(\varphi)) - r_{ab}^2)/(r_{ab}^2\,r_{bc}^2) & & \\
F_{3b-2\,3c-1} & = 1/r_{bc}^2 & & \\
F_{3b-1\,3b-1} & = -2\sin(\varphi)\cos(\varphi)/r_{ab}^2 & & \\
F_{3b-1\,3c-2} & = 1/r_{bc}^2 & & \\
F_{3b\,3b} & = ((r_{ab} + r_{bc}\cos(\varphi) - 2r_{ab}\,r_{bc})/(r_{ab}^2\,r_{bc}\sin(\varphi)) & & \\
F_{3b\,3c} & = (r_{bc} - r_{ab}\cos(\varphi))/(r_{ab}\,r_{bc}^2\sin(\varphi)) & & \\
F_{3c-2\,3c-1} & = -1/r_{bc}^2 & & \\
F_{3c\,3c} & = \cos(\varphi)/(r_{bc}^2\sin(\varphi)) & &
\end{array}
$$

Torsion angle ϑ

$$
\begin{aligned}
\vartheta(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c, \boldsymbol{r}_d) = {} & \operatorname{sgn}((\boldsymbol{r}_b - \boldsymbol{r}_a)\,((\boldsymbol{r}_c - \boldsymbol{r}_b) \times (\boldsymbol{r}_d - \boldsymbol{r}_b))) \\
& \arccos(((\boldsymbol{r}_b - \boldsymbol{r}_a) \times (\boldsymbol{r}_c - \boldsymbol{r}_a))\,((\boldsymbol{r}_c - \boldsymbol{r}_b) \times (\boldsymbol{r}_d - \boldsymbol{r}_b)) \\
& /(r_{ab}\, r_{bc}^2\, r_{bd} \sin(\varphi) \sin(\delta)))
\end{aligned}
$$

$$\varphi(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c) = \arccos((\boldsymbol{r}_a - \boldsymbol{r}_b)\,(\boldsymbol{r}_c - \boldsymbol{r}_b)/(r_{ab}\, r_{bc})),\ 0 < \varphi < \pi$$

$$\delta(\boldsymbol{r}_b, \boldsymbol{r}_c, \boldsymbol{r}_d) = \arccos((\boldsymbol{r}_c - \boldsymbol{r}_b)\,(\boldsymbol{r}_d - \boldsymbol{r}_b)/(r_{bc}\, r_{bd})),\ 0 < \delta < \pi$$

$$
\begin{array}{llll}
u_1 & = y^c - y^b,\ v_1 = x^c - x^b & & \\
\sin(\alpha) & = -\sin(\arctan(u_1/v_1)) & & v_1 < 0 \\
\sin(\alpha) & = -1 & u_1 < 0, & v_1 = 0 \\
\sin(\alpha) & = 0 & u_1 = 0, & v_1 = 0 \\
\sin(\alpha) & = 1 & u_1 > 0, & v_1 = 0 \\
\sin(\alpha) & = \sin(\arctan(u_1/v_1)) & & v_1 > 0 \\
\cos(\alpha) & = \cos(\arctan(u_1/v_1)) & & v_1 < 0 \\
\cos(\alpha) & = 0 & u_1 \neq 0, & v_1 = 0 \\
\cos(\alpha) & = 1 & u_1 = 0, & v_1 = 0 \\
\cos(\alpha) & = -\cos(\arctan(u_1/v_1)) & & v_1 > 0 \\
u_2 & = z^c - z^b,\ v_2 = \cos(\alpha)\,(x^c - x^b) - \sin(\alpha)\,(y^c - y^b) & & \\
\sin(\beta) & = \sin(\arctan(u_2/v_2)) & & v_2 < 0 \\
\sin(\beta) & = 1 & u_2 < 0, & v_2 = 0 \\
\sin(\beta) & = -1 & u_2 > 0, & v_2 = 0 \\
\cos(\beta) & = \cos(\arctan(u_2/v_2)) & & v_2 < 0 \\
\cos(\beta) & = 0 & & v_2 = 0 \\
u_3 & = \cos(\beta)\,(z^d - z^b) - \sin(\beta)\,(\cos(\alpha)\,(x^d - x^b) - \sin(\alpha)\,(y^d - y^b)) & & \\
v_3 & = \sin(\alpha)\,(x^d - x^b) + \cos(\alpha)\,(y^d - y^b) & & \\
\sin(\gamma) & = \sin(\arctan(u_3/v_3)) & & v_3 < 0 \\
\sin(\gamma) & = -\sin(\arctan(u_3/v_3)) & & v_3 \geq 0 \\
\cos(\gamma) & = -\cos(\arctan(u_3/v_3)) & & v_3 < 0 \\
\cos(\gamma) & = \cos(\arctan(u_3/v_3)) & & v_3 \geq 0
\end{array}
$$

$$
\begin{aligned}
E_{3a-1} &= -\sin(\vartheta)/(r_{ab} \sin(\varphi)) \\
E_{3a} &= \cos(\vartheta)/(r_{ab} \sin(\varphi)) \\
E_{3b-1} &= (r_{bc} - r_{ab} \cos(\varphi)) \sin(\vartheta)/(r_{ab}\, r_{bc} \sin(\varphi)) \\
E_{3b} &= ((r_{ab} \cos(\varphi) - r_{bc}) \cos(\vartheta)/(r_{ab} \sin(\varphi)) + (r_{bc} - r_{bd} \cos(\delta))/(r_{bd} \sin(\delta)))/r_{bc} \\
E_{3c-1} &= \cos(\varphi) \sin(\vartheta)/(r_{bc} \sin(\varphi)) \\
E_{3c} &= (\cos(\delta)/\sin(\delta) - \cos(\varphi) \cos(\vartheta)/\sin(\varphi))/r_{bc} \\
E_{3d} &= -1/(r_{bd} \sin(\delta)) \\
F_{3a-2\,3b-1} &= \sin(\vartheta)/(r_{ab}\, r_{bc} \sin(\varphi)) \\
F_{3a-2\,3b} &= -\cos(\vartheta)/(r_{ab}\, r_{bc} \sin(\varphi)) \\
F_{3a-2\,3c-1} &= -\sin(\vartheta)/(r_{ab}\, r_{bc} \sin(\varphi)) \\
F_{3a-2\,3c} &= \cos(\vartheta)/(r_{ab}\, r_{bc} \sin(\varphi))
\end{aligned}
$$

$$F_{3a-1\,3a-1} = 2\sin(\vartheta)\cos(\vartheta)/(r_{ab}^2 \sin^2(\varphi))$$
$$F_{3a-1\,3a} = (2\sin^2(\vartheta) - 1)/(r_{ab}^2 \sin^2(\varphi))$$
$$F_{3a-1\,3b-1} = 2(r_{ab}\cos(\varphi) - r_{bc})\sin(\vartheta)\cos(\vartheta)/(r_{ab}^2 r_{bc} \sin^2(\varphi))$$
$$F_{3a-1\,3b} = (r_{ab}\cos(\varphi) - r_{bc})(2\sin^2(\vartheta) - 1)/(r_{ab}^2 r_{bc}\sin^2(\varphi))$$
$$F_{3a-1\,3c-1} = -2\cos(\varphi)\sin(\vartheta)\cos(\vartheta)/(r_{ab} r_{bc}\sin^2(\varphi))$$
$$F_{3a-1\,3c} = \cos(\varphi)(1 - 2\sin^2(\vartheta))/(r_{ab} r_{bc}\sin^2(\varphi))$$
$$F_{3a\,3a} = -2\sin(\vartheta)\cos(\vartheta)/(r_{ab}^2\sin^2(\varphi))$$
$$F_{3a\,3b-1} = (r_{ab}\cos(\varphi) - r_{bc})(2\sin^2(\vartheta) - 1)/(r_{ab}^2 r_{bc}\sin^2(\varphi))$$
$$F_{3a\,3b} = 2(r_{bc} - r_{ab}\cos(\varphi))\sin(\vartheta)\cos(\vartheta)/(r_{ab}^2 r_{bc}\sin^2(\varphi))$$
$$F_{3a\,3c-1} = \cos(\varphi)(1 - 2\sin^2(\vartheta))/(r_{ab} r_{bc}\sin^2(\varphi))$$
$$F_{3a\,3c} = 2\cos(\varphi)\sin(\vartheta)\cos(\vartheta)/(r_{ab} r_{bc}\sin^2(\varphi))$$
$$F_{3b-2\,3b-1} = (r_{ab}\cos(\varphi) - r_{bc})\sin(\vartheta)/(r_{ab} r_{bc}^2\sin(\varphi))$$
$$F_{3b-2\,3b} = ((r_{bc} - r_{ab}\cos(\varphi))\cos(\vartheta)/(r_{ab}\sin(\varphi)) + (r_{bd}\cos(\delta) - r_{bc}) \\ /(r_{bd}\sin(\delta)))/r_{bc}^2$$
$$F_{3b-2\,3c-1} = (r_{bc} - r_{ab}\cos(\varphi))\sin(\vartheta)/(r_{ab} r_{bc}^2\sin(\varphi))$$
$$F_{3b-2\,3c} = ((r_{ab}\cos(\varphi) - r_{bc})\cos(\vartheta)/(r_{ab}\sin(\varphi)) + (r_{bc} - r_{bd}\cos(\delta)) \\ /(r_{bd}\sin(\delta)))/r_{bc}^2$$
$$F_{3b-1\,3b-1} = ((r_{ab}\cos(\varphi) - r_{bc})^2 + r_{ac}^2)\sin(\vartheta)\cos(\vartheta)/(r_{ab}^2 r_{bc}^2\sin^2(\varphi))$$
$$F_{3b-1\,3b} = (r_{ac}^2(2\sin^2(\vartheta) - 1)/(r_{ab}^2\sin^2(\varphi)) - \sin^2(\vartheta) + r_{cd}^2/(r_{bd}^2\sin^2(\delta)))/r_{bc}^2$$
$$F_{3b-1\,3c-2} = -\cos(\varphi)\sin(\vartheta)/(r_{bc}^2\sin(\varphi))$$
$$F_{3b-1\,3c-1} = (r_{ab}(\sin^2(\varphi) - 2) + 2r_{bc}\cos(\varphi))\sin(\vartheta)\cos(\vartheta)/(r_{ab} r_{bc}^2\sin^2(\varphi))$$
$$F_{3b-1\,3c} = (\sin^2(\vartheta) + (r_{bc}\cos(\varphi) - r_{ab})(2\sin^2(\vartheta) - 1)/(r_{ab}\sin^2(\varphi)) \\ + (r_{bc}\cos(\delta) - r_{bd})/(r_{bd}\sin^2(\delta)))/r_{bc}^2$$
$$F_{3b-1\,3d} = (r_{bd}\cos(\delta) - r_{bc})/(r_{bc} r_{bd}^2\sin^2(\delta))$$
$$F_{3b\,3b} = ((r_{ab}\cos(\varphi) - r_{bc})^2 + r^2{}_{ac})\sin(\vartheta)\cos(\vartheta)/(r^2{}_{ab} r^2{}_{bc}\sin^2(\varphi))$$
$$F_{3b\,3c-2} = (\cos(\varphi)\cos(\vartheta)/\sin(\varphi) - \cos(\delta)/\sin(\delta))/r_{bc}^2$$
$$F_{3b\,3c-1} = (\sin^2(\vartheta) + (r_{bc}\cos(\varphi) - r_{ab})(2\sin^2(\vartheta) - 1)/(r_{ab}\sin^2(\varphi)) \\ + (r_{bc}\cos(\delta) - r_{bd})/(r_{bd}\sin^2(\delta)))/r_{bc}^2$$
$$F_{3b\,3c} = (r_{ab}(2 - \sin^2(\varphi)) - 2r_{bc}\cos(\varphi))\sin(\vartheta)\cos(\vartheta)/(r_{ab} r_{bc}^2\sin^2(\varphi))$$
$$F_{3b\,3d-2} = 1/(r_{bc} r_{bd}\sin(\delta))$$
$$F_{3b\,3d-1} = (r_{bd}\cos(\delta) - r_{bc})/(r_{bc} r_{bd}^2\sin^2(\delta))$$
$$F_{3c-2\,3c-1} = \cos(\varphi)\sin(\vartheta)/(r_{bc}^2\sin(\varphi))$$
$$F_{3c-2\,3c} = (\cos(\delta)/\sin(\delta) - \cos(\varphi)\cos(\vartheta)/\sin(\varphi))/r_{bc}^2$$
$$F_{3c-1\,3c-1} = (2 - \sin^2(\varphi))\sin(\vartheta)\cos(\vartheta)/(r_{bc}^2\sin^2(\varphi))$$
$$F_{3c-1\,3c} = ((2\sin^2(\vartheta) - 1)/\sin^2(\varphi) - \sin^2(\vartheta) + 1/\sin^2(\delta))/r_{bc}^2$$
$$F_{3c-1\,3d} = -\cos(\delta)/(r_{bc} r_{bd}\sin^2(\delta))$$
$$F_{3c\,3c} = (\sin^2(\varphi) - 2)\sin(\vartheta)\cos(\vartheta)/(r_{bc}^2\sin^2(\varphi))$$
$$F_{3c\,3d-2} = -1/(r_{bc} r_{bd}\sin(\delta))$$
$$F_{3c\,3d-1} = -\cos(\delta)/(r_{bc} r_{bd}\sin^2(\delta))$$
$$F_{3d-1\,3d} = 1/(r_{bd}^2\sin^2(\delta))$$

Out of plane angle τ

$\tau(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c, \boldsymbol{r}_d) = \arcsin((\boldsymbol{r}_a - \boldsymbol{r}_b)\,((\boldsymbol{r}_c - \boldsymbol{r}_b) \times (\boldsymbol{r}_d - \boldsymbol{r}_b))/(r_{ab}\, r_{bc}\, r_{bd} \sin(\delta)))$
$\quad - \pi/2 < \tau < \pi/2$

$\delta(\boldsymbol{r}_b, \boldsymbol{r}_c, \boldsymbol{r}_d) = \arccos((\boldsymbol{r}_c - \boldsymbol{r}_b)\,(\boldsymbol{r}_d - \boldsymbol{r}_b)/(r_{bc}\, r_{bd})),\ 0 < \delta < \pi$

$u_1 = y^c - y^b,\ v_1 = x^c - x^b$

$\sin(\alpha) = -\sin(\arctan(u_1/v_1))$		$v_1 < 0$
$\sin(\alpha) = -1$	$u_1 < 0,$	$v_1 = 0$
$\sin(\alpha) = 0$	$u_1 = 0,$	$v_1 = 0$
$\sin(\alpha) = 1$	$u_1 > 0,$	$v_1 = 0$
$\sin(\alpha) = \sin(\arctan(u_1/v_1))$		$v_1 > 0$
$\cos(\alpha) = \cos(\arctan(u_1/v_1))$		$v_1 < 0$
$\cos(\alpha) = 0$	$u_1 \neq 0,$	$v_1 = 0$
$\cos(\alpha) = 1$	$u_1 = 0,$	$v_1 = 0$
$\cos(\alpha) = -\cos(\arctan(u_1/v_1))$		$v_1 > 0$

$u_2 = z^c - z^b,\ v_2 = \cos(\alpha)\,(x^c - x^b) - \sin(\alpha)\,(y^c - y^b)$

$\sin(\beta) = \sin(\arctan(u_2/v_2))$		$v_2 < 0$
$\sin(\beta) = 1$	$u_2 < 0,$	$v_2 = 0$
$\sin(\beta) = -1$	$u_2 > 0,$	$v_2 = 0$
$\sin(\beta) = \cos(\arctan(u_2/v_2))$		$v_2 < 0$
$\cos(\beta) = 0$		$v_2 = 0$

$u_3 = \cos(\beta)\,(z^d - z^b) - \sin(\beta)\,(\cos(\alpha)\,(x^d - x^b) - \sin(\alpha)\,(y^d - y^b))$

$v_3 = \sin(\alpha)\,(x^d - x^b) + \cos(\alpha)\,(y^d - y^b)$

$\sin(\gamma) = \sin(\arctan(u_3/v_3))$	$v_3 < 0$
$\sin(\gamma) = -\sin(\arctan(u_3/v_3))$	$v_3 \geq 0$
$\cos(\gamma) = -\cos(\arctan(u_3/v_3))$	$v_3 < 0$
$\cos(\gamma) = \cos(\arctan(u_3/v_3))$	$v_3 \geq 0$

$\varphi(\boldsymbol{r}_a, \boldsymbol{r}_b, \boldsymbol{r}_c) = \arccos((\boldsymbol{r}_a - \boldsymbol{r}_b)\,(\boldsymbol{r}_c - \boldsymbol{r}_b)/(r_{ab}\, r_{bc}))$

$h_\tau = \mathrm{sgn}(((\boldsymbol{r}_b - \boldsymbol{r}_a) \times (\boldsymbol{r}_c - \boldsymbol{r}_a))\,(\boldsymbol{r}_c - \boldsymbol{r}_b) \times (\boldsymbol{r}_d - \boldsymbol{r}_b)))\,(1 - \cos^2(\varphi)/\cos^2(\tau))^{1/2}$

$E_{3a-2} = \cos(\varphi)\sin(\tau)/(r_{ab}\cos(\tau))$

$E_{3a-1} = -h_\tau \sin(\tau)/r_{ab}$

$E_{3a} = -\cos(\tau)/r_{ab}$

$E_{3b-2} = -\cos(\varphi)\sin(\tau)/(r_{ab}\cos(\tau))$

$E_{3b-1} = h_\tau \sin(\tau)/r_{ab}$

$E_{3b} = \cos(\tau)/r_{ab} + ((r_{bd}\cos(\delta) - r_{bc})h_\tau/(r_{bd}\sin(\delta)) - \cos(\varphi)/\cos(\tau))/r_{bc}$

$E_{3c} = \cos(\varphi)/\cos(\tau) - h_\tau \cos(\delta)/\sin(\delta))/r_{bc}$

$E_{3d} = h_\tau/(r_{bd}\sin(\delta))$

$F_{3a-2\,3a-2} = (2\cos^2(\varphi) - h_\tau^2)\sin(\tau)/(r_{ab}^2\cos(\tau))$

$F_{3a-2\,3a-1} = -\cos(\varphi)h_\tau^2 \sin(\tau)\,(2 + 1/\cos^2(\tau))/r_{ab}^2$

$F_{3a-2\,3a} = \cos(\varphi)\,(1/\cos(\tau) - 2\cos(\tau))/r_{ab}^2$

$$F_{3a-2\,3b-2} = (h_\tau^2 - 2\cos^2(\varphi))\sin(\tau)/(r_{ab}^2\cos(\tau))$$
$$F_{3a-2\,3b-1} = \cos(\varphi)h_\tau\sin(\tau)\,(2 + 1/\cos^2(\tau))/r_{ab}^2$$
$$F_{3a-2\,3b} = ((2r_{bc}\cos(\varphi)\cos(\tau) + (r_{ab}h_\tau^2 - r_{bc}\cos(\varphi))/\cos(\tau))/r_{ab} + (r_{bd}\cos(\delta) - r_{bc})\cos(\varphi)h_\tau/(r_{bd}\sin(\delta)\cos^2(\tau)))/(r_{ab}r_{bc})$$
$$F_{3a-2\,3c} = -(h_t + \cos(\varphi)\cos(\delta)/(\sin(\delta)\cos(\tau)))h_\tau/(r_{ab}r_{bc})\cos(\tau))$$
$$F_{3a-2\,3d} = \cos(\varphi)h_\tau/(r_{ab}r_{bd}\sin(\delta)\cos^2(\tau))$$
$$F_{3a-1\,3a-1} = (2\cos(\tau) - \cos^2(\varphi)\,(2 + 1/\cos^2(\tau))/\cos(\tau))\sin(\tau)/r_{ab}^2$$
$$F_{3a-1\,3a} = h_\tau(2\cos^2(\tau) - 1)/r_{ab}^2$$
$$F_{3a-1\,3b-2} = \cos(\varphi)h_\tau\sin(\tau)\,(2 + 1/\cos^2(\tau))/r_{ab}^2$$
$$F_{3a-1\,3b-1} = (\cos^2(\varphi)\,(2 + 1/\cos^2(\tau))\cos(\tau) - 2\cos(\tau))\sin(\tau)/r_{ab}^2$$
$$F_{3a-1\,3b} = ((r_{bc}(1 - 2\cos^2(\tau)) + r_{ab}\cos(\varphi)/\cos^2(\tau))h_\tau/r_{ab} + (r_{bd}\cos(\delta) - r_{bc})\cos^2(\varphi)/(r_{bd}\sin(\delta)\cos^3(\tau)))/(r_{ab}r_{bc})$$
$$F_{3a-1\,3c} = -\cos(\varphi)\,(h_\tau + \cos(\varphi)\cos(\delta)/(\sin(\delta)\cos(\tau)))/(r_{ab}r_{bc})\cos^2(\tau))$$
$$F_{3a-1\,3d} = \cos^2(\varphi)/(r_{ab}r_{bd}\sin(\delta)\cos^3(\tau))$$
$$F_{3a\,3a} = -2\sin(\tau)\cos(\tau)/r_{ab}^2$$
$$F_{3a\,3b-2} = \cos(\varphi)\,(2\cos(\tau) - 1/\cos(\tau))/r_{ab}^2$$
$$F_{3a\,3b-1} = h_\tau(1 - 2\cos^2(\tau))/r_{ab}^2$$
$$F_{3a\,3b} = 2\sin(\tau)\cos(\tau)/r_{ab}^2$$
$$F_{3b-2\,3b-2} = (2\cos^2(\varphi) - h_\tau^2)\sin(\tau)/(r_{ab}^2\cos(\tau))$$
$$F_{3b-2\,3b-1} = -\cos(\varphi)h_\tau\sin(\tau)\,(2 + 1/\cos^2(\tau))/r_{ab}^2$$
$$F_{3b-2\,3b} = ((((r_{ab}^2 + r_{bc}^2)\cos(\varphi) - r_{ab}r_{bc}h_\tau^2)\cos(\tau) - 2r_{bc}^2\cos(\varphi)\cos(\tau)) /r_{ab} + (r_{ab} + r_{bc}\cos(\varphi)/\cos^2(\tau))\,(r_{bc} - r_{bd}\cos(\delta))h_\tau /(r_{bd}(\sin(\delta)))/(r_{ab}r_{bc}^2)$$
$$F_{3b-2\,3c} = ((r_{ab}(r_{bd}\cos(\delta) - r_{bc}) + r_{bc}r_{bd}\cos(\varphi)\cos(\delta)/\cos^2(\tau))h_\tau /(r_{bd}\sin(\delta)) + (r_{bc}h_\tau^2 - r_{ab}\cos(\varphi))/\cos(\tau))/(r_{ab}r_{bc}^2)$$
$$F_{3b-2\,3d} = -\cos(\varphi)h_\tau/(r_{ab}r_{bd}\sin(\delta)\cos^2(\tau))$$
$$F_{3b-1\,3b-1} = (2\cos(\tau) - \cos^2(\varphi)\,(2 + 1/\cos^2(\tau))/\cos(\tau))\sin(\tau)/r_{ab}^2$$
$$F_{3b-1\,3b} = (((r_{ab}^2 + r_{bc}^2(2\cos^2(\tau) - 1))r_{bd}^2 - r_{ab}(r_{ab}r_{cd}^2/\sin^2(\delta) + r_{bc}r_{bd}^2\cos(\varphi)/\cos^2(\tau)))h_\tau/(r_{ab}r_{bd}) + (r_{ab} - r_{bc}\cos(\varphi)/\cos^2(\tau))\,(r_{bd}\cos(\delta) - r_{bc})\cos(\varphi) /(\sin(\delta)\cos(\tau)))/(r_{ab}r_{bc}^2r_{bd})$$
$$F_{3b-1\,3c} = (((r_{bc}\cos(\varphi)/\cos^2(\tau) - r_{ab})r_{bd} + r_{ab}(r_{bd} - r_{bc}\cos(\delta)) /\sin^2(\delta))h_\tau/r_{bd} + (r_{bc}\cos(\varphi)/\cos^2(\tau) - r_{ab})\cos(\varphi)\cos(\delta) /(\sin(\delta)\cos(\tau)))/(r_{ab}r_{bc}^2)$$
$$F_{3b-1\,3d} = ((r_{bc} - r_{bd}\cos(\delta))h_\tau/(r_{bd}\sin(\delta)) + (r_{ab} - r_{bc}\cos(\varphi)/\cos^2(\tau)) \cos(\varphi)/(r_{ab}\cos(\tau)))/(r_{bc}r_{bd}\sin(\delta))$$
$$F_{3b\,3b} = (2(r_{bc} - r_{bd}\cos(\delta))\cos(\varphi)h_\tau/\sin(\delta)\cos^2(\tau)) - (2r_{bc}^2r_{bd}^2\cos(\tau) + r_{ab}^2(r_{bd}^2 - (2r_{bd}^2 - r_{cd}^2/\sin^2(\delta))\cos^2(\varphi) /\cos^2(\tau))/\cos(\tau))/(r_{ab}^2r_{bd}))\sin(\tau)/(r_{bc}^2r_{bd})$$
$$F_{3b\,3c-2} = (h_\tau\cos(\delta)/\sin(\delta) - \cos(\varphi)/\cos(\tau))/r_{bc}^2$$

$$F_{3b\,3c-1} = (r_{bd}\cos(\delta) - r_{bc})\,(h_\tau\cos(\delta)/\sin(\delta) - \cos(\varphi)/\cos(\tau)) /(r_{bc}^2\, r_{bd}\sin(\delta))$$

$$F_{3b\,3c} = (r_{bd} - (2r_{bd} + (r_{bc}\cos(\delta) - r_{bd})/\sin^2(\delta))\cos^2(\varphi)/\cos^2(\tau) + (2r_{bd}\cos(\delta) - r_{bc})\cos(\varphi)\,h_\tau/\sin(\delta)\cos(\tau)))\sin(\tau) /(r_{bc}^2\, r_{bd}\cos(\tau))$$

$$F_{3b\,3d-2} = -h_\tau/(r_{bc}\, r_{bd}\sin(\delta))$$

$$F_{3b\,3d-1} = (r_{bc} - r_{bd}\cos(\delta))h_\tau/(r_{bc}\, r_{bd}^2\sin^2(\delta))$$

$$F_{3b\,3d} = ((r_{bc} - r_{bd}\cos(\delta))\cos(\varphi)/(r_{bd}^2\sin(\delta)\cos(\tau)) - h_\tau)\cos(\varphi) \sin(\tau)/(r_{bc}\, r_{bd}\sin(\delta)\cos^2(\tau))$$

$$F_{3c-2\,3c} = (\cos(\varphi)/\cos(\tau) - h_\tau\cos(\delta)/\sin(\delta))/r_{bc}^2$$

$$F_{3c-1\,3c} = (\cos(\varphi)/\cos(\tau) - h_\tau\cos(\delta)/\sin(\delta))\cos(\delta)/(r_{bc}^2(\delta))$$

$$F_{3c-1\,3d} = (h_\tau\cos(\delta)/\sin(\delta) - \cos(\varphi)/\cos(\tau))/(r_{bc}\, r_{bd}\sin(\delta))$$

$$F_{3c\,3c} = (\cos^2(\varphi)\,(2 - 1/\sin^2(\delta))/\cos^2(\tau) - 1 - 2\cos(\varphi)\,h_\tau\cos(\delta) /(\sin(\delta)\cos(\tau)))\sin(\tau)/(r^2{}_{bc}\cos(\tau))$$

$$F_{3c\,3d-2} = h_\tau/(r_{bc}\, r_{bd}\sin(\delta))$$

$$F_{3c\,3d-1} = h_\tau\cos(\delta)/(r_{bc}\, r_{bd}\sin^2(\delta))$$

$$F_{3c\,3d} = \cos(\varphi)\,(h_\tau + \cos(\varphi)\cos(\varphi)/(\sin(\delta)\cos(\tau)))\sin(\tau) /(r_{bc}\, r_{bd}\,\sin(\delta)\cos^2(\tau))$$

$$F_{3d-1\,3d} = -h_\tau/(r_{bd}^2\sin^2(\delta))$$

$$F_{3d\,3d} = -\cos^2(\varphi)\,\sin(\tau)/(r_{bd}^2\sin^2(\delta)\cos^3(\tau))$$

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