Cartesian coordinates reconstruction from CP puckering parameters

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Starting remarks

Formulas for the reconstruction of the cartesian coordinates for six-membered ring molecules with known CP puckering parameters will be settled. The reconstruction algorithm is taken from [2]. Some code details are supplied.

Formulas are given for the special case of six–membered ring. Formulas that are needed to be encoded are the numbered one.

1 From CP to (x_j, y_j, z_j)

It's not possible to reconstruct all the 18 cartesian coordinates having only the 3 puckering parameters (Q, θ, ϕ) or equivalently (q_2, ϕ_2, q_3). It's necessary to supplement these information with the set of bond lenghts and bond angles of the ring.

Following Ref. [2] the reconstruction can be done in five step:

1. Calculation of z_j elevations;
2. Projection of bond lenghts/angles on the mean plane;
3. Ring partition;
4. Ring partition's coordinates calculation;
5. Ring atoms coordinates calculation.

1.1 Calculation of z_j elevations

It's the only operation that directly involves the puckering parameters. The inversion formula

$$z_j = \frac{1}{\sqrt{3}} q_2 \cos\left[\phi_2 + \frac{2\pi(j-1)}{3}\right] + \frac{1}{\sqrt{6}} q_3 (-1)^{j-1} \tag{1}$$

$$= Q\left\{\frac{1}{\sqrt{3}} \sin\theta \cos\left[\phi + \frac{2\pi(j-1)}{3}\right] + \frac{1}{\sqrt{6}} \cos\theta (-1)^{j-1}\right\} \tag{2}$$

(from Ref. [1]) gives the elevation of the atoms with respect to the CP mean plane.

1.2 Projection of bond lenghts/angles on the mean plane

Since the puckering information has been yet transferred from the puckering coordinates to the z_j coordinates, it's sufficient to project all the other data (bond lenghts r_{ij} and the bond angles β_{ijk}, see Sec. 2 for suitable default values) onto the mean plane to reconstruct only the planar shadow of the ring. From Ref. [2] we have the projections

$$r_{ij} \rightarrow \qquad r'_{ij} = \sqrt{r_{ij}^2 - (z_j - z_i)^2} \tag{3}$$

$$\beta_{ijk} \rightarrow \quad \cos\beta'_{ijk} = \frac{(z_k - z_i)^2 - (z_j - z_i)^2 - (z_k - z_j)^2 + 2 r_{ij} r_{jk} \cos\beta_{ijk}}{2 r'_{ij} r'_{jk}} \tag{4}$$

with $i, j, k = 1, \ldots, 6$.

1.3 Ring partition

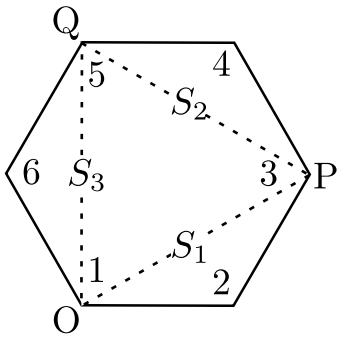

Figure 1: Ring partition

The ring is now divided into three parts, identifying three sections for the subsequent calculations. According to Fig. 1, in order to work with the S_n segments only parts of the supplied data are needed at each segment, namely

$$\begin{aligned} S_1 &= \{1,2,3\} \quad \text{needs} \quad r'_{12}, r'_{23}, \beta'_{123} \\ S_2 &= \{3,4,5\} \quad \text{needs} \quad r'_{34}, r'_{45}, \beta'_{345} \\ S_3 &= \{5,6,1\} \quad \text{needs} \quad r'_{56}, r'_{61}, \beta'_{561} \end{aligned}$$

(all 6 bond lenght and 3 bond angles). For future use, we collect the lenght of the segments S_n, namely

$$|\overline{OP}| = \sqrt{(r'_{12})^2 + (r'_{23})^2 - 2r'_{12}r'_{23}\cos\beta'_{123}} \tag{5}$$

$$|\overline{QP}| = \sqrt{(r'_{34})^2 + (r'_{45})^2 - 2r'_{34}r'_{45}\cos\beta'_{345}} \tag{6}$$

$$|\overline{OQ}| = \sqrt{(r'_{56})^2 + (r'_{61})^2 - 2r'_{56}r'_{61}\cos\beta'_{561}} \tag{7}$$

The segments S_n, and their endpoints O, P, and Q, are the skeleton for the ring reconstruction.

1.4 Ring partition's coordinates calculation

The segments S_n can be now aligned in the arbitrary planar frame $Ox'y'$ (as shown in Fig. 2) in which we can collect the coordinates $(x'_i, y'_i)_{S_n}$ of the i-th atom.

Atoms $\{1,2,3\} \in S_1$ are now located at

$$1_{S_1} \equiv O = \begin{pmatrix} 0 \\ 0 \end{pmatrix}_{S_1} \quad , \quad 2_{S_1} = \begin{pmatrix} -r'_{12} \\ 0 \end{pmatrix}_{S_1} \tag{8}$$

$$3_{S_1} \equiv P_{S_1} = \begin{pmatrix} -r'_{12} + r'_{23}\cos\beta'_{123} \\ r'_{23}\sin\beta'_{123} \end{pmatrix}_{S_1} \tag{9}$$

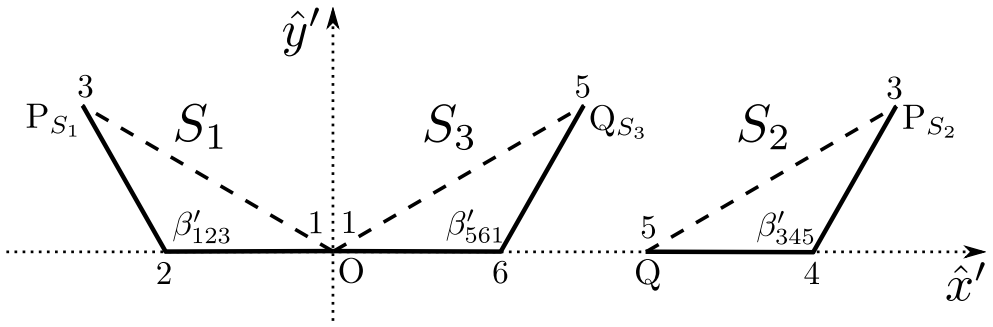

Figure 2: Atoms coordinates

Atoms $\{3, 4, 5\} \in S_2$ are now located at

$$5_{S_2} \equiv Q = \begin{pmatrix} |\overline{OQ}| \\ 0 \end{pmatrix}_{S_2} \quad , \quad 4_{S_2} = \begin{pmatrix} |\overline{OQ}| + r'_{45} \\ 0 \end{pmatrix}_{S_2} \tag{10}$$

$$3_{S_2} \equiv P_{S_2} = \begin{pmatrix} |\overline{OQ}| + r'_{45} - r'_{34}\cos\beta'_{345} \\ r'_{34}\sin\beta'_{345} \end{pmatrix}_{S_2} \tag{11}$$

Atoms $\{5, 6, 1\} \in S_3$ are now located at

$$1_{S_3} \equiv O = \begin{pmatrix} 0 \\ 0 \end{pmatrix}_{S_3} \quad , \quad 6_{S_3} = \begin{pmatrix} r'_{61} \\ 0 \end{pmatrix}_{S_3} \tag{12}$$

$$5_{S_3} \equiv Q_{S_3} = \begin{pmatrix} r'_{61} - r'_{56}\cos\beta'_{561} \\ r'_{56}\sin\beta'_{561} \end{pmatrix}_{S_3} \tag{13}$$

1.5 Ring atoms coordinates calculation

The previous coordinates has only to be rotated properly in order to complete the reconstruction. Namely, a proper rotation matrix

$$\mathcal{R}_A(\phi) = \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix}$$

($R_A(\phi)$ is a counterclockwise rotation of angle ϕ around the pole A) is needed for each S_n segments. The procedure follows three steps.

1.5.1 Point P real position and angles for rotations

It's necessary to know how to rebuild the triangle OPQ to be the skeleton for the ring. In Fig. 3 points P_{S_1} and P_{S_2} has to be rotated to reach the

position P for the reconstruction. The vertex P of the OPQ triangle can be localized solving the system

$$\begin{cases} x^2 + y^2 = \overline{OP}^2 & \text{(circle of center } O \text{ and radius } \overline{OP}) \\ (x - \overline{OQ})^2 + y^2 = \overline{PQ}^2 & \text{(circle of center } Q \text{ and radius } \overline{PQ}) \end{cases} \tag{14}$$

Eventually, taking the solution with $y > 0$, the intersection is at

$$x_P = \frac{\overline{OP}^2 + \overline{OQ}^2 - \overline{PQ}^2}{2\overline{OQ}} \quad , \quad y_P = \sqrt{\overline{OP}^2 - \frac{(\overline{OP}^2 + \overline{OQ}^2 - \overline{PQ}^2)^2}{4\overline{OQ}^2}} \tag{15}$$

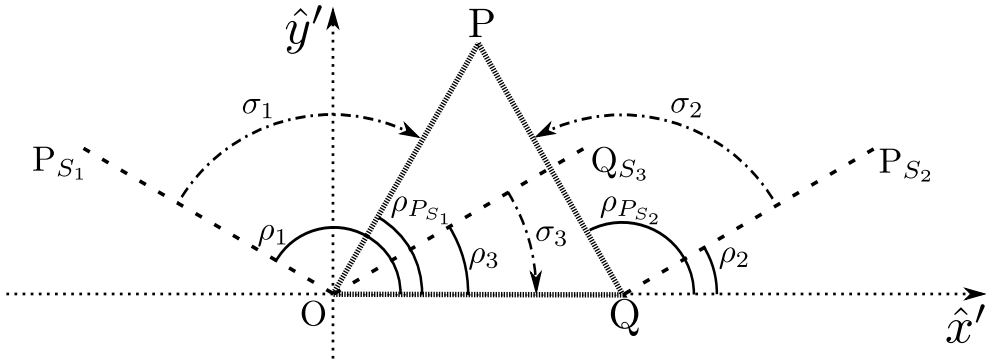

Figure 3: P position and rotation angles

The starting alignement of S_n segments gives angular elevations ρ_n such that

$$\tan\rho_1 = \frac{y_{P_{S_1}}}{x_{P_{S_1}}} = \frac{r'_{23}\sin\beta'_{123}}{-r'_{12} + r'_{23}\cos\beta'_{123}} \tag{16}$$

$$\tan\rho_2 = \frac{y_{P_{S_2}}}{(x_{P_{S_2}} - \overline{OQ})} = \frac{r'_{34}\sin\beta'_{345}}{r'_{45} - r'_{34}\cos\beta'_{345}} \tag{17}$$

$$\tan\rho_3 = \frac{y_{Q_{S_3}}}{x_{Q_{S_3}}} = \frac{r'_{56}\sin\beta'_{561}}{r'_{61} - r'_{56}\cos\beta'_{561}} \tag{18}$$

while P localization gives $\overline{OP}$ and $\overline{QP}$ segment elevations with respect to the x axe such that

$$\tan\rho_{P_{S_1}} = \frac{y_P}{x_P} \tag{19}$$

$$\tan\rho_{P_{S_2}} = \frac{y_P}{x_P - \overline{OQ}} \tag{20}$$

(see Fig. 3 for angles definition and Sec. 2 for the implementation).

1.5.2 Reconstruction of the ring on OPQ triangle

Now we can identify the proper rotation $\mathcal{R}_A(\phi)$ that maps the points P_{S_1} and P_{S_2} onto P and the point Q_{S_2} onto Q. The rotation needed (see Fig. 3) are the following:

i) S_1 has to be rotated clockwise around O by angle $\sigma_1 = |\rho_1 - \rho_{P_{S_1}}|$

ii) S_2 has to be rotated counterclockwise around Q by angle $\sigma_2 = |\rho_{P_{S_2}} - \rho_2|$

iii) S_3 has to be rotated clockwise around O by angle $\sigma_3 = |\rho_3|$

In this way the coordinates $\vec{R}'_j = \begin{pmatrix} x_j \\ y_j \end{pmatrix}$ are[1]

$$\vec{R}'_1 \equiv O = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{21}$$

$$\vec{R}'_2 = \mathcal{R}_O(-\sigma_1)2_{S_1} = \mathcal{R}_O(-\sigma_1) \begin{pmatrix} -r'_{12} \\ 0 \end{pmatrix}_{S_1} \tag{22}$$

$$\vec{R}'_3 \equiv P = \begin{pmatrix} x_P \\ y_P \end{pmatrix} = \begin{pmatrix} \frac{\overline{OP}^2 + \overline{OQ}^2 - \overline{PQ}^2}{2\overline{OQ}} \\ \sqrt{\overline{OP}^2 - \frac{(\overline{OP}^2 + \overline{OQ}^2 - \overline{PQ}^2)^2}{4\overline{OQ}^2}} \end{pmatrix} \tag{23}$$

$$\vec{R}'_4 = \begin{pmatrix} \overline{OQ} \\ 0 \end{pmatrix} + \mathcal{R}_Q(\sigma_2) \left[\begin{pmatrix} |\overline{OQ}| + r'_{45} \\ 0 \end{pmatrix}_{S_2} - \begin{pmatrix} \overline{OQ} \\ 0 \end{pmatrix}_{S_2} \right] \tag{24}$$

$$\vec{R}'_5 \equiv Q = \begin{pmatrix} \overline{OQ} \\ 0 \end{pmatrix} \tag{25}$$

$$\vec{R}'_6 = \mathcal{R}_O(-\sigma_3)6_{S_3} = \mathcal{R}_O(-\sigma_3) \begin{pmatrix} r'_{61} \\ 0 \end{pmatrix}_{S_3} \tag{26}$$

1.5.3 Final roto-translation

Now with the $\vec{R}'_j$ vector we can calculate the geometric center G of the ring projection onto the mean plane

$$\vec{R}'_G = \sum_{j=1}^{6} \vec{R}'_j \tag{27}$$

[1] for checking purpose can be calculated also

$$P = \mathcal{R}_O(-\sigma_1)3_{S_1} = \mathcal{R}_Q(\sigma_2)3_{S_2} \quad , \quad Q = \mathcal{R}_O(-\sigma_3)5_{S_3}$$

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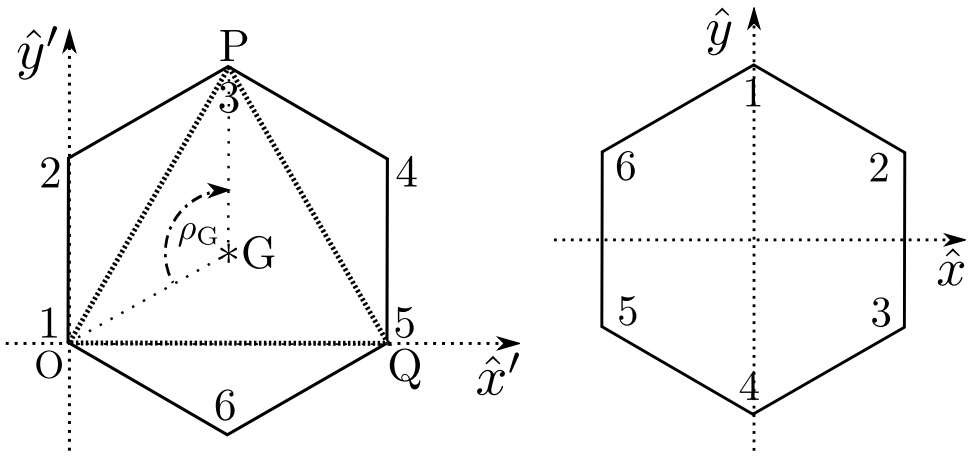

(a) geometric center G location

(b) final ring atom positions (planar view)

Figure 4: Final transformation

and the angle between the y' axe and the segment $\overline{OG}$, that is

$$\tan\left[\rho_G - \frac{\pi}{2}\right] = \frac{y_G}{x_G} \tag{28}$$

(see Fig. 4(a) for angle definition).

We are now ready to calculate the final coordinates of the atoms in the reference frame of the mean plane $\{\hat{\mathrm{l}}, \hat{\mathrm{m}}, \hat{\mathrm{n}}\}$ as defined in the definition of the CP coordinates (see Ref. [1]). What we need is to translate the origin of the $x'y'$ frame from O to G and rotate all the atoms in such way that the atom 1 will be along the y' axe, namely a clockwise rotation around G by angle ρ_G. Thus, we will have

$$\vec{R}_j = \begin{pmatrix} x_j \\ y_j \end{pmatrix} = \mathcal{R}_G(-\rho_G)\left(\vec{R}'_j - \vec{R}'_G\right) \tag{29}$$

that gives the final coordinates (x_j, y_j) (see Fig. 4(b) for the result) with which we can construct the full posistion vectors

$$\mathbf{R}_j = x_j\hat{\mathrm{l}} + y_j\hat{\mathrm{m}} + z_j\hat{\mathrm{n}}$$

of the ring atoms.

2 Code details

Some remarks are needed for coding the previous formulas.

- suitable/realistic values fo the CP coordinates (Q, θ, ϕ) or (q_2, ϕ_2, q_3) has to be supplied, otherwise the algorithm gives `nan` results;
- default values for r_{ij} and β_{ijk} data can be setted up from the ideal values of a cyclohexane molecule, which has (fixed) bond lenght $r_{ij} \equiv b$ and (fixed) bond angles $\beta_{ijk} \equiv \nu$. Standard values are $b = 1.54$ Å and ν as the exact tetrahedral angles of an sp^3 hybridized carbon which has $\cos \nu = -1/3$;
- the inversion of all $\tan \alpha$ functions has to be done using implementation of $\arctan[\tan \alpha]$ that gives answers in $[0, 2\pi]$, such as `atan2`;

References

[1] Cremer D., Pople J.A., General definition of ring puckering coordinates, J. Am. Chem. Soc., 1975, vol 97, 1354–1358

[2] Cremer D., Calculation of puckered rings with analytical gradients, Journal of Physical Chemistry, 1990, vol 94, 5502–5509