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Divergence-Free Description of Molecular Rotation in Cartesian Coordinates: Derivation of the Axis-Rotation Formula and Application to Molecular Modelling

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ABSTRACT

The methods of Euler angles and unit quaternions are typically used to represent the rotations and the orientation of a rigid body in space. Based on some algebraic manipulations, the alternative formula, called axis-rotation, which describes the rotation around a given axis with an arbitrary angle, is derived. The use of some of its applications in several fields of molecular modelling is introduced. Although we present the use of the axis-rotation formula only in some fields of the molecular simulation, it is applicable in any other domain where object rotation is employed.

1. INTRODUCTION

Molecules are composed of numbers of atoms, ranging from dimers, e.g. HF, to very big complex systems of hundred thousands of atoms, e.g. big proteins or DNA. Atoms are bound to molecules by intra-atomic potentials, which give rise to mutual atomic motions like vibrations, bending motions or torsions. In the case of dynamical calculations, the applied time step has to be chosen small enough in order resolve the fastest motions in the systems. For the case of molecular dynamics simulations, where electronic degrees of freedom are neglected and the motion of atoms is described classically, the timestep of integration is usually in the range of ≈1fs. On the other hand, in the case of Monte Carlo simulations, the number of trial moves has to be chosen large enough in order to sample the configuration space, accessible by the molecule. However, often one is not interested particularly in short time but in long time dynamics of a molecule or a whole system composed of molecules, e.g. folding of a protein into a native state or transport phenomena in liquids. Taking into account the fastest vibrational motions in the system explicitly implies a computational burden. Therefore, as a first approximation, the fastest degrees of freedom are often frozen and mutual distances between neighboured atoms are fixed to their average distance[1] (further approximations may also freeze bending or torsional motions). If all degrees of freedom in a molecule are constrained, the dynamics is described as rigid body motion (we note that handling constant distances between objects is also an important item in very much different areas, e.g. computer graphics, computer games, spacecraft- and car-simulations or robotics). The motion of a rigid body can naturally been splitted into translational motion of the center of mass and rotational motion around its principal axes, i.e. all atoms belonging to the same molecule rotate an angle $\mathrm{d}\varphi$ around the same axis and have the same angular velocity $\boldsymbol{\omega}$. The equations of translational and rotational motion thereby describe the reaction of the rigid body to external forces. The motion will be constant, conserving total energy and angular momentum if no external forces act on the body.

The graphical interfaces allow the interactive modification of the atomic structures by selecting fragments of structures and manipulating them by translation, rotation, projection and scaling. The rotation is a fundamental tool in building and merging of the atomic structures as molecules, clusters, crystals and surfaces. It can be used also in the conversion from internal coordinates to cartesian coordinates, which are required by some codes of the different branches of the molecular simulations.

In order to describe the orientation and rotation in space of a rigid body, two mathematical tools are usually used: the Euler angles and the quaternions.[2,18] The method of Euler angles consists of three successive rotations around the x-, y- and z-axes, with three angles ϕ, θ and ψ, called Euler angles. Different sets of Euler angle rotations exist and the three rotations may be applied in any order. Quaternions are mathematical objects that generalize the complex numbers and obey the Pawley algebra.[3] Formally, a quaternion $\mathbf{q}=\left(q_0,\mathbf{q}_v\right)^T$ is a vector with four components, one scalar component, q_0, and a vectorial one $\mathbf{q}_v=(q_1,q_2,q_3)^T$.[4] The quaternion with the form $\mathbf{q}=(\cos(\varphi/2), \mathbf{n}\sin(\varphi/2))^T$ is normalized $q_0^2+q_1^2+q_2^2+q_3^2=1$ and is associated to the rotation of the angle φ around the unit axis $\mathbf{n}=(n_1,n_2,n_3)^T$.[5] The components of the quaternions are expressed as products of sine and cosine functions of the Euler angles and Euler angles and quaternions can be mutually transformed into each other.[18]

The equations of motion based on Euler angles contain terms with singularities for some particular orientations. This problem may be overcome either by some successive rotations of smaller angles or by changing the coordinate system when approaching the singularity. Both solutions require some additional statements in the algorithm and introduce some computational overhead. The advantage of the quaternion description is that there are no special cases for the orientation of a molecule, but the method is not free of problems, as the norm of the quaternions is not conserved along the evolution in time.[6] The accumulation of the numerical errors may be prevented by normalization of the quaternions at each time step. The Euler angle method provides a physical description of rigid body rotation around an axis. In contrast, the quaternion formalism completely describes the rotation but they are mathematical objects that do not reflect directly the physical meaning of the rotation.

The third possible way to describe the rotation of a rigid body around an axis is the so-called axis-rotation formula.[7-10] For unknown reason, it is not popular in the field of molecular simulations and as far we know, it is mentioned only in one article.[11] This formula may be derived from the quaternion formalism but it can be directly obtained by the decomposition of the vector position in the perpendicular and parallel components to the rotation axis. The axis-rotation formula provides a clear picture of the rotation with any angle ($\varphi \in \mathbb{R}$) around any axis $\mathbf{n}$ in space. In this article we are concerned with the derivation of the axis-rotation formula and some applications of it. It allows a simple geometrical manipulation of the molecules or molecular fragments, which is a great facility for the preparation of the coordinates of the molecular systems for the input in Quantum Chemistry calculations, Molecular Dynamics and Monte-Carlo simulations. The rotational dynamics of the rigid bodies may be recovered and analysed from the trajectories of the component particles. Furthermore, the axis-rotation formula helps to construct the symmetry operators in the point group theory.

2. BUILDING AND MERGING MOLECULES

2.1. ROTATION OF A POINT AROUND AN AXIS

Let us consider the changes of the coordinates of a point after the rotation with the angle φ around an arbitrary axis, described by the unit vector $\mathbf{n}$, that is going through the point O described by the vector $\boldsymbol{\rho}_0$ with respect to the origin of a given coordinate reference frame. Two points, two real or dummy atoms, a bond or a direction (for example the electric dipole, the principal inertia axis or the angular velocity) may define the rotation axis. The direction of rotation is given by the right-hand rule: the thumb of the right hand is oriented in the direction of the vector $\mathbf{n}$ and the curl of the fingers gives the positive direction of rotation.

The vectors $\boldsymbol{\rho} = \boldsymbol{\rho}_0 + \mathbf{r}$ and $\boldsymbol{\rho}' = \boldsymbol{\rho}_0 + \mathbf{r}'$ give the position of a point P before and after the rotation, respectively. A simple formula that relates $\mathbf{r}'$ to $\mathbf{r}$ (the relative vectors to $\boldsymbol{\rho}_0$, after and before rotations, respectively) is derived in the Appendix A1 and it is:

$$\mathbf{r}'=\mathbf{r}\cos\varphi+\mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r})(1-\cos\varphi)+\mathbf{n}\times\mathbf{r}\sin\varphi. \tag{1}$$

Mathematically, we may write the right-hand rule as $\mathbf{n}(\mathbf{r}\times\mathbf{r}')>0$. The case $\mathbf{n}(\mathbf{r}\times\mathbf{r}')<0$ is equivalent to a negative angle $\varphi < 0$, which means that the rotation is done in the inverse direction.

The transformation of the relative position to O is given by $\mathbf{r}' = \hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}\mathbf{r}$, where

$$\hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}=\cos\varphi\hat{\mathbf{I}}+(1-\cos\varphi)\mathbf{n}(\mathbf{n}^{\mathrm{T}}\hat{\mathbf{I}})+\sin\varphi\mathbf{n}\times\hat{\mathbf{I}} \tag{2}$$

is the associated rotation operator and $\hat{\mathbf{I}}$ represents the identity operator that transforms a vector in itself $\hat{\mathbf{I}}\mathbf{r}=\mathbf{r}$. Therefore, the absolute position of the point P after rotation is described by

$$\boldsymbol{\rho}' = \boldsymbol{\rho}_0 + \hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}(\boldsymbol{\rho} - \boldsymbol{\rho}_0). \tag{3}$$

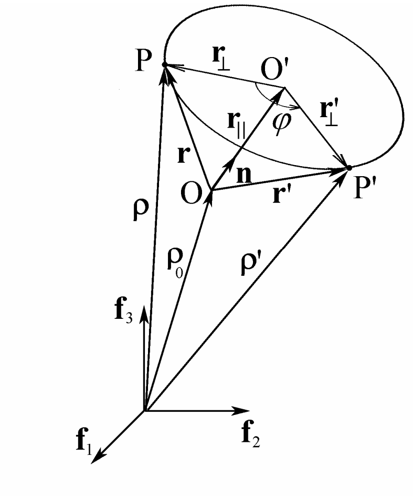

Fig 1. The definition of the absolute (greek bold letters) and of the relative (bold letters) position vectors, before and after the rotation of the point P to P' by the angle φ around the unit axis $\mathbf{n}$ which is going through the reference point O. The vectors $\{\mathbf{f}_i\}_{i=1,3}$ are the unit vectors of the absolute reference frame.

The evolution in time of any point $\boldsymbol{\rho}$ is decomposed into the translational motion of a reference point O described by the vector $\boldsymbol{\rho}_0$ and the rotation around the axis going through the reference point:

$$\dot{\boldsymbol{\rho}} = \dot{\boldsymbol{\rho}}_0 + \dot{\mathbf{r}} \qquad (4)$$

where,

$$\dot{\mathbf{r}} = \omega\mathbf{n}\times\mathbf{r} = \boldsymbol{\omega}\times\mathbf{n} \qquad (5)$$

describes the rotation around the axis $\mathbf{n} = \boldsymbol{\omega}/\omega$ with the angular velocity $\boldsymbol{\omega}$ (see the Appendix A2). Because of the separating of the vectors from the static (3) and dynamic equations (4) in the one component that refer to the reference frame and another inside it, it appears useful to introduce the local reference frame for the arbitrary point O. The axes of the local reference frame are parallel to the axes of the absolute reference frame and move together with the reference point O. In the further considerations we will refer only to the rotational part, around an axis that is going through a point O. In case of a set of atoms, the center of mass of the system is the most convenient choice for the reference point O.

Here we list some properties of the rotation operator associated to the arbitrary unit vector $\mathbf{n}$:

i) $\hat{\mathbf{R}}_{\mathbf{n}}^{\alpha}\hat{\mathbf{R}}_{\mathbf{n}}^{\beta} = \hat{\mathbf{R}}_{\mathbf{n}}^{\alpha+\beta} = \hat{\mathbf{R}}_{\mathbf{n}}^{\beta}\hat{\mathbf{R}}_{\mathbf{n}}^{\alpha}$, the rotations around the same axis are commutative;

ii) $\hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}\hat{\mathbf{R}}_{\mathbf{n}}^{-\varphi} = \hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}\hat{\mathbf{R}}_{\mathbf{-n}}^{\varphi} = \hat{\mathbf{R}}_{\mathbf{n}}^{0} = \hat{\mathbf{I}}$ and therefore the inverse operator is $(\hat{\mathbf{R}}_{\mathbf{n}}^{\varphi})^{-1} = \hat{\mathbf{R}}_{\mathbf{n}}^{-\varphi} = \hat{\mathbf{R}}_{\mathbf{-n}}^{\varphi}$;

iii) $\hat{\mathbf{R}}_{\mathbf{n}}^{\pi} = -\hat{\mathbf{I}} + 2\mathbf{n}(\mathbf{n}^{\mathrm{T}}\hat{\mathbf{I}})$;[12]

iv) $(\hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}\mathbf{a})(\hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}\mathbf{b}) = \mathbf{ab}$, $(\hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}\mathbf{a})\times(\hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}\mathbf{b}) = \hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}(\mathbf{a}\times\mathbf{b})$, the dot product and the cross product of the two arbitrary vectors $\mathbf{a}$ and $\mathbf{b}$ are preserved;

v) $\mathbf{n}$ is the eigenvector of the rotation operator $\hat{\mathbf{R}}_{\mathbf{n}}^{\varphi}\mathbf{n} = \mathbf{n}$ for the eigenvalue 1, which is natural because the rotation operator does not change the rotation axis.

In case of the manipulation of the molecules or fragments of the chemical systems, it is more economical to construct the rotation matrix:

$$\mathbf{R} = \begin{bmatrix} n_1n_1(1\text{-}\cos\varphi)+\cos\varphi & n_1n_2(1\text{-}\cos\varphi)\text{-}n_3\sin\varphi & n_1n_3(1\text{-}\cos\varphi)+n_2\sin\varphi \\ n_1n_2(1\text{-}\cos\varphi)+n_3\sin\varphi & n_2n_2(1\text{-}\cos\varphi)+\cos\varphi & n_2n_3(1\text{-}\cos\varphi)\text{-}n_1\sin\varphi \\ n_1n_3(1\text{-}\cos\varphi)\text{-}n_2\sin\varphi & n_2n_3(1\text{-}\cos\varphi)+n_1\sin\varphi & n_3n_3(1\text{-}\cos\varphi)+\cos\varphi \end{bmatrix} \qquad (6)$$

and to multiply it with the coordinates of the atoms that are rotated (see eq. 29, Appendix A3).

2.2. ALIGNMENT OF MOLECULES INTO A DIRECTION

In the graphic visualization, in the crystal surface construction or in the set up of the initial structure of a chemical system, very often fragments or the full system must be oriented under an angle θ formed by a given direction from the system described by the unit vector $\mathbf{d}$ and a fixed direction in space described by the unit vector $\mathbf{d_0}$ (see Fig. 2). Two atoms, a bond, the dipole moment, the normal to a plane or a special direction from space may determine each direction. The current angle formed by the two directions is measured as $\theta_0 = \arccos(\mathbf{dd}_0)$, in the direction of superposing $\mathbf{d}$ over $\mathbf{d}_0$. The system has to be rotated by angle $\theta_0 - \theta$ around the unit axis $\mathbf{n} = \dfrac{\mathbf{d}\times\mathbf{d}_0}{|\mathbf{d}\times\mathbf{d}_0|}$. Therefore, it is translated with the mass center in the reference point O, it is rotated and translated back with the mass center in the initial position. For example, this procedure can be applied to display a system with a special direction $\mathbf{d}$ perpendicular to the screen or when an adsorbed molecule must be oriented with the dipole moment to make the angle θ with the normal of a surface.

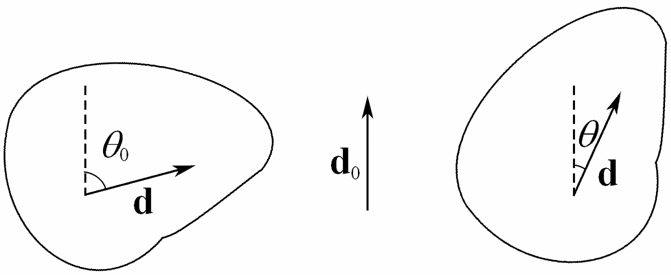

Fig 2. A rigid-body in initial orientation and after its reorientation to form the angle θ between the direction **d** fixed on the body and the given direction in space $\mathbf{d}_0$.

Some of the chemical system properties can be easier determined considering the symmetry of system. Programs that employ the symmetry of the molecule require the coordinates of the molecule to be given in so-called standard symmetry orientation, which is defined based on the rules: (i) if the system has a symmetry C_s then the z axis is chosen perpendicular to the symmetry plane; (ii) if the system has symmetry axes then the z axis is oriented along the axis with the highest order; (iii) the x axis is considered in one vertical plane if it exists or along an axis C_2 if it exists. The procedure presented above can be applied to orient a given system in the standard symmetry orientation.

3. CONVERSION BETWEEN INTERNAL AND CARTESIAN COORDINATES

The molecular simulation codes start the calculations from the identity of the atoms and their position in space described by their cartesian coordinates (CC) or their mutual relative position described by the internal coordinates (IC). The chemical systems are graphically visualized based on the cartesian coordinates of the constitutive atoms. For a molecule of N atoms, there are 3N cartesian coordinates necessary to specify the location of the atoms. The standard molecular geometries, determined by the averaging of the interatomic distances, of the bond angles and of the dihedral angles provided by different experiments and different substances with similar atomic environments, constitute a good starting point in constructing the molecular geometries in the ICs. Moreover, the graphical programs offer the possibility to monitor the construction of molecules by a two-dimensional drawing of the molecule, which establish the connections between atoms. Based on the connectivity of the atoms in the molecule, the geometry of a non-linear molecule can be represented by *3N-6* internal coordinates (*N-1* bond distances, *N-2* bond angles and *N-3* dihedral angles). Three degrees of freedom that define the center of mass position, and other three that, describe the orientation of the molecule are not considered, the position and orientation of the molecule, being fixed by the first three atoms. The distance between the atoms 1-2 and 2-3 and the bond angle 1-2-3 defines the positions of the first three atoms. For a linear molecule, N-1 distances determine the relative positions of the atoms. The place and the orientation in space of the molecule is defined by the position of any two atoms.

The shapes of the potential energy surfaces are different in the cartesian and internal coordinates, generally being more complicated in the first case. Depending on the size and on the topology of the system, the optimization convergence is dependent on the type of coordinates. As a rule, the optimization in ICs is faster, except for large molecules or molecules with some particular topologies (cyclic, planar or linear). Providing a good initial hessian, especially when the geometry is far from equilibrium, the optimization in CC is enforced, making comparable the convergence in both types of coordinates.

In the empirical force fields, the different components of the energy are expressed as functions of the interatomic distances, bond and dihedral angles, the displacements of the atoms are determined in CC. Therefore, in Molecular Mechanics and Molecular Dynamics calculations the cartesian coordinates are mainly employed although there are some approaches to apply internal coordinates in Molecular Dynamics simulations. In principle, in Monte-Carlo simulations there are no problems to use the ICs, but the calculations are usually done in CCs.

The transform of the coordinates from a type to another is very often demanded. The cartesian to internal conversion is direct. Based on the inter-atomic distance, the connectivity of the atoms is established. From the positions of the first three atoms, the distances between the atoms 1-2 and 2-3 and the bond angle 1-2-3 are determined. For other atoms L=4,N the internal coordinates are determined in successive iterations for each atom L. The distance between the atoms K and L is given by $d_{KL} = |\mathbf{r}_{KL}| = |\boldsymbol{\rho}_L - \boldsymbol{\rho}_K|$, where the vectors $\boldsymbol{\rho}_{K,L}$ are the position vectors of the atoms K and L and $\mathbf{r}_{KL}$ is the relative vector of L to K. The angle formed by the three connected atoms J-K-L is given by $\alpha_{JKL} = \pi - \arccos\left(\mathbf{a}\cdot\frac{\mathbf{r}_{KL}}{\mathbf{r}_{KL}}\right)$, where the vector $\mathbf{a} = \mathbf{r}_{JK}/|\mathbf{r}_{JK}|$ is the unit vector along the J-K bond (see Fig. 3). The dihedral angle formed by four successive connected atoms is given by $\beta_{IJKL} = \arccos(\frac{\mathbf{uv}}{|\mathbf{u}||\mathbf{v}|})$, where $\mathbf{u} = \mathbf{r}_{JI} - (\mathbf{r}_{JI}\mathbf{a})\mathbf{a}$ and $\mathbf{v} = \mathbf{r}_{KL} - (\mathbf{r}_{KL}\mathbf{a})\mathbf{a}$ are the perpendicular components to the bond J-K of the vectors $\mathbf{r}_{JI}$ and $\mathbf{r}_{KL} = \boldsymbol{\rho}_L - \boldsymbol{\rho}_K$. The vectors $\mathbf{r}_{JI} = \boldsymbol{\rho}_I - \boldsymbol{\rho}_J$ and $\mathbf{r}_{JK} = \boldsymbol{\rho}_K - \boldsymbol{\rho}_J$ are the relative positions of atoms I and K with respect to the atom J.

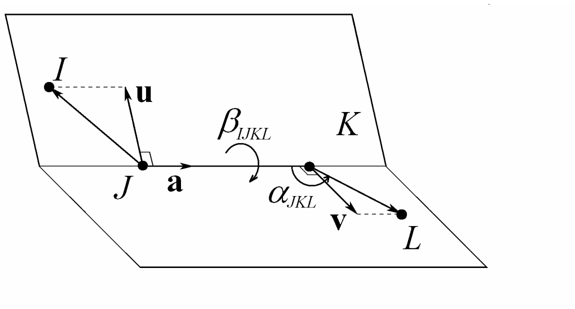

Fig 3. The definition of the internal coordinates for a set of four chemical bonded atoms I, J, K and L.

The inverse transform, from the internal to the cartesian coordinates requires more computational effort and employs three rotations around the three axes of the coordinates of each atom L=4,N, where N is the number of atoms of the system. Here we present a procedure that requires only two rotations for each atom L=4,N. For large N and for very often-used conversion internal-cartesian this procedure reduces significantly the computational effort. The first atom may occupy any position in space (usually it is placed in the origin of the reference frame), the second atom is placed around the atom 1 at a distance d_{12} (usually along a reference frame axis) and the third one is positioned at the distance d_{23} from the atom 2, along the bond 1-2. After that the atom 3 is rotated around an axis perpendicular to the bond 1-2 by the angle $\alpha_{123}-\pi$. The angle α_{123} is the desired angle to be formed by the bonds 1-2 and 2-3. Because the plane formed by the first three atoms is arbitrarily oriented in space, the rotation axis may be any one perpendicular to the bond 1-2. Usually, this plane is chosen to coincide with one plane formed by two axes of the reference frame and in this case the rotation axis is the third axis. The positions of the other atoms are successively determined, based on the positions of the other three connected atoms that are already settled. Thus the position of the each next atom *L* is established based on the length d_{LK} of the bond formed with another atom *K*, the angle α_{JKL} of the two bonds *J-K* and *K-L* that share the same central atom *K* and the dihedral angle β_{IJKL} formed by four sequentially bonded atoms *I-J-K-L* which is the angle necessary to rotate the (*J*,*K*,*L*) plane over the plane (*I*,*J*,*K*) (see Fig. 4). We will use the vectors **u** and **a** defined above (see Fig. 3) and the unit vector $\mathbf{b} = \dfrac{\mathbf{u}\times\mathbf{a}}{|\mathbf{u}\times\mathbf{a}|}$, which is the normal of the plane (*I*,*J*,*K*). Let us consider the point *X* along the axis *J-K* from *J* to *K* at the distance d_{KL} from the atom *K*: $\mathbf{r}_{KX} = \mathbf{a}\cdot d_{KL}$. Now the point *X* is rotated in the plane (*I*,*J*,*K*) to the point *Y* with the angle $\pi-\alpha_{JKL}$ around the axis **b**: $\mathbf{r}_{KY} = \mathbf{R}_{\mathbf{b}}^{\alpha_{JKL}-\pi}\mathbf{r}_{KX}$. The point Y is rotated around the axis **a** with the angle $\pi-\beta_{IJKL}$ to the final position of the atom *L*: $\mathbf{r}_{KL} = \mathbf{R}_{\mathbf{a}}^{\beta_{IJKL}-\pi}\mathbf{r}_{KY}$. The absolute position of the atom *L* is $\boldsymbol{\rho}_L = \boldsymbol{\rho}_K + \mathbf{r}_{KL}$. The cycle is repeated for each atom, considered as *L*, until the coordinates of the all atoms are determined.

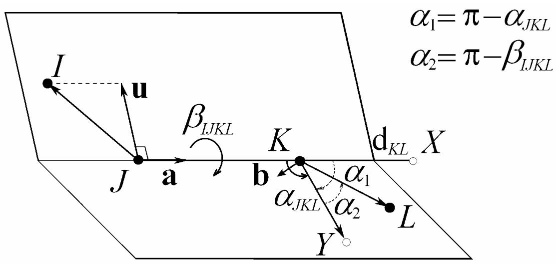

Fig 4. The determination of the position of the atom *L* when the position of other three bonded atoms is known.

4. MERGING OF TWO STRUCTURES

There are situations when the geometries of two fragments or two molecules are known and we have to merge them to create a new structure. The relative positioning of the two structures S1 and S2 is determined by the distance between their mass center and by their relative orientation. When the two systems must be connected by a chemical bond, let say formed between the atoms *J* from S1 and *K* from S2, the relative positioning of the two structures is given by the relative arrangement of the two atoms *I* and *J* from S1 to the two atoms *K* and *L* from S2: the distance d_{JK} between the two connected atoms *J* and *K*, the angles α_{IJK} and α_{JKL} and the dihedral angle β_{IJKL} (see Fig. 5). To assure the distance d_{JK} between *J* and *K*, all the atoms of the system S2 are translated with $\boldsymbol{\rho}_J - d_{JK}\cdot\dfrac{\mathbf{r}_{JK}}{|\mathbf{r}_{JK}|}$, where $\mathbf{r}_{JK} = \boldsymbol{\rho}_K - \boldsymbol{\rho}_J$ is the position of the atom *K* relative to the position of the atom *J* before the translation. In the new position the system S2 is rotated around the axis that is going through the atom J and is perpendicular to the plane determined by the atoms *I*, *J* and *K* with the angle $\alpha^{o}_{IJK} - \alpha_{IJK}$, where α^{o}_{IJK} is the angle formed by the atoms *I*, *J* and *K* before the rotation. To settle the angle α_{JKL}, the system S2 is again rotated around an axis that is going through K and is perpendicular to the plane determined by the atoms *J*, *K* and *L*, with the angle $\alpha^{o}_{JKL}-\alpha_{JKL}$, where α^{o}_{JKL} is the angle before the rotation. To fix the dihedral angle, the current angle β^{o}_{IJKL} is determined and the system S2 is rotated around the axis **a** that coincides with the direction *I-J*, with the angle $\beta^{o}_{IJKL}-\beta_{IJKL}$.

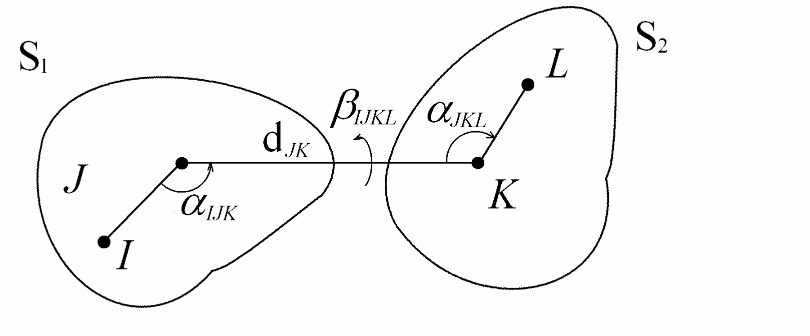

Fig 5. The definition of the relative orientation parameters (d_{JK}, α_{IJK},α_{JKL} and β_{IJKL}) of the two atomic structures S1 and S2.

When the torsion angle β_{IJKL} is not predetermined, the stable conformers are established determining the torsion angle which corresponds to the local minimums of the energy: one fragment is rotated around the axis *J-K* using the axis-rotation formula by an incremental angle and the dependency of the total energy function on the torsion angle is recorded. For a higher accuracy, the internal geometries of the two fragments are optimized for each torsion angle β_{IJKL}.

4.1. ORIENTATION OF A SYSTEM

The principal inertia axes $\{\mathbf{f}_i\}_{i=1,3}$, relative to the a given reference point O, of a chemical system characterize the spatial arrangement of the constituent atoms in the local reference frame with the origin in O. Let us suppose that the eigenvalues and the corresponding eigenvectors are ordered as $I_1 \leq I_2 \leq I_3$. The zero eigenvalue of $I_1 = 0$ indicates that the atoms are arranged along the principal axis $\mathbf{f}_1$. The other two principal moments are equals $I_2 = I_3$ and the corresponding eigenvalues are any two orthogonal vectors that are perpendicular to the molecule. If the first eigenvalue is much smaller than the other two $I_1 << I_2 \leq I_3$, then the eigenvector $\mathbf{f}_1$ still points the orientation of the molecule and the value of I_1 is a measure of the deviation of the atoms from a linear molecule. When the atoms are arranged in a plane, the principal inertia moments satisfy the relation $I_3 = I_1 + I_2$. The deviation from this relation characterizes the deviation from the average plane of the atoms. The principal axis $\mathbf{f}_3$ is the normal of the plane and the other two principal axes are contained in the plane determined by the atoms.

When a molecule is rotated in space with the angle φ around an axis **n,** which is going through the reference point O, the inertia matrix is changed as $\mathbf{I}' = \mathbf{R}\mathbf{I}\mathbf{R}^T$, where **R** is the corresponding rotation matrix (see Eq. (6)). The new principal axes $\{\mathbf{f}_i'\}_{i=1,3}$ can be determined calculating $\mathbf{I}'$ and solving the eigenvalues and eigenvectors equation. It is easier to determine the new principal axes directly by the rotation of the initial principal axes $\{\mathbf{f}_i\}_{i=1,3}$: $\mathbf{f}_i' = \mathbf{R}\mathbf{f}_i$ (see Fig. 6). When the chemical system is the subject of some successive rotations it is not necessary to calculate the coordinates of the atoms after each rotation. The new values of the principal axes after each rotation are calculated and from the relative orientation of the last principal axis and the initial principal axis, the total rotation matrix is determined as it is indicated in Appendix A3. Finally using the total rotation matrix the coordinates of the atoms can be established.

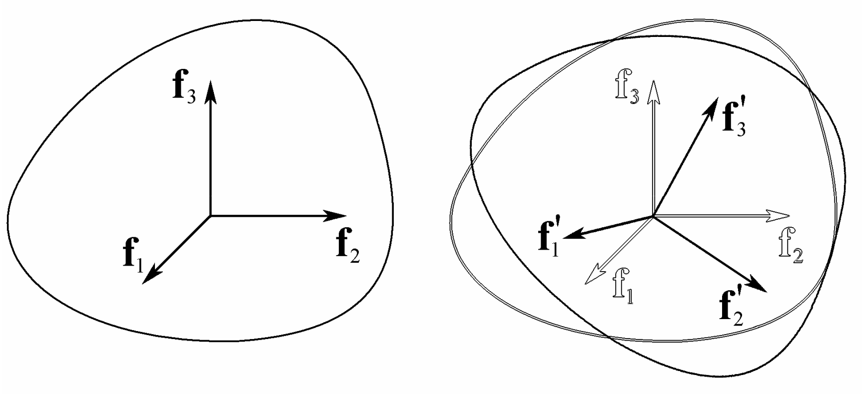

Fig 6. The body reference frames of a rigid-body before (left) and after his rotation (right). The vectors $\{\mathbf{f}_i\}_{i=1,3}$ and $\{\mathbf{f}_i\}_{i=1,3}$ are the principal inertia axes of the rigid-body before and after rotation.

4.2. RELATIVE ORIENTATION OF TWO SYSTEMS

The alignment of two systems is an important problem. The adsorption of a molecule in an active site on a surface implies a good geometrical matching between the parts of the molecule and the surface that are responsible for the frontier orbitals. A similar situation occurred in case of the drug interaction with the receptor proteins. The two systems may be optimised as a whole system but because of the large number of degrees, the calculation effort can be reduced studying in the first approximation, the alignment between the target molecule and the template keeping rigid the two systems. The two similar molecules or parts of molecules can be superposed by successive rotations, minimizing the least-squares differences between the root-mean-squares coordinates of the two structures. The mass centers of the two structures are made coincident with the origin of the coordinate frame. The starting relative arrangement of the two structures is usually determined by the identification of a set of three pairs of corresponding atoms in the two structures. The bonds between the first and the second selected atoms of each molecule are made collinear. Finally, the third selected atoms of each molecule are put in the same plane. In the case of the different geometries of the two structures we may reduce the number of iterations, making coincident the principle inertial axis of the two structures by the axis-rotation following the procedure presented in the Appendix A3. After the fit, one structure is displaced from the origin of the coordinate frame back to the initial position.

4.3. RECOVERING ROTATIONAL INFORMATION OF MOLECULES FROM ATOM TRAJECTORIES

There are situations in which the trajectories of the atoms are previously obtained from the Molecular Dynamics simulation and we are interested to extract information on the rotational motion of the molecules. For each time step, the principal inertia axes are determined and the rotation axes and the rotation angle are determined from the change of the principle axes between the two time steps following the procedure presented in the Appendix A3. The vectors of the basis set $\{\mathbf{f}_i\}_{i=1,3}$ are the principal inertia axes of a molecule at the time step t_0 and $\{\mathbf{f}_i\,'\}_{i=1,3}$ are the principal inertia axes of the same molecule at the next time step $t_0+\Delta t$. In case of the flexible molecules the vibrational motion contaminates the rotation motion determined in this way. This undesired effect could be eliminated by averaging the motion on a proper chosen number of time steps *n*, centerd on the time step t_0 and on the time step $t_0+n\Delta t$.

4.4. APPLICATIONS TO SYMMETRY

Based on the concepts of the group theory, the symmetry of the molecules may be exploited to obtain qualitative information on molecules. This information allows us to select appropriate basis sets, to classify them and to find the very important selection rules for the transitions in the electronic and the vibration spectra. Moreover, the symmetry properties can be used to reduce significantly the computational efforts by block-diagonalization of the matrices that describe the interaction in the chemical system.

The simple and general analytic formula of the axis-rotation operator allow us to build the other symmetry operators which work for any orientation of the chemical system (it is not necessary to use the standard symmetry orientation) and for high symmetry molecules (like dodecahedron or icosahedron). The symmetry operators do not affect the mass center of the molecule and in case that the molecule presents inversion symmetry, the inversion point coincides with the molecule mass center. Therefore, without to restrict the generality of the operators formulas, the reference point O used to define the rotation is chosen to be the mass center.

The axis-rotation operator corresponding to an axis $\mathbf{n}$ and to a quantized angle $\varphi_n = \dfrac{2\pi}{n}$ gives the rotation symmetry operator $\hat{\mathbf{C}}_{\mathbf{n}}^{n}$ of degree *n* in respect to the axis $\mathbf{n}$ as

$$\hat{\mathbf{C}}_{\mathbf{n}}^{n} = \cos\varphi_n \hat{\mathbf{I}} + (1-\cos\varphi_n)\mathbf{n}(\mathbf{n}^{\mathrm{T}}\hat{\mathbf{I}}) + \sin\varphi_n \mathbf{n}\times\hat{\mathbf{I}} \qquad (7)$$

The reflection operator with respect to a symmetry plane with normal $\mathbf{n}$ that is going through the mass center is given by

$$\hat{\boldsymbol{\sigma}}_{\mathbf{n}} = \hat{\mathbf{I}} - 2\mathbf{n}(\mathbf{n}^{\mathrm{T}}\hat{\mathbf{I}}) \qquad (8)$$

that correspond to the rotation operator with π radians, around an axis that is going through O and it is included in the symmetry plane.

The rotation-reflection operator is determined by the composition of a rotation operator with respect to the axis $\mathbf{n}$ that is going through the mass center and a reflection operator with respect to a plane that contains the mass center and has as normal the unit vector $\mathbf{n}$,

$$\hat{\mathbf{S}}_{\mathbf{n}}^{n} = \cos\varphi_n \hat{\mathbf{I}} - (1+\cos\varphi_n)\mathbf{n}(\mathbf{n}^{\mathrm{T}}\hat{\mathbf{I}}) + \sin\varphi_n \mathbf{n}\times\hat{\mathbf{I}} \qquad (9)$$

The inversion operator of a point described by $\mathbf{r}$ with respect to a point O is

$$\hat{\mathbf{I}}_{inv} = -\hat{\mathbf{I}} \qquad (10)$$

which transform $\mathbf{r}$ in $\mathbf{-r}$.

Numerous algorithms are developed for determination of the symmetry of an object.[13] We do not insist here on this topic but we mention that the operators presented above are very helpful to detect the symmetry elements. The procedure may be speed-up using the fact that the symmetry of the molecule is reflected in some properties of the structure like the dipole moment and the composition of the inertia tensor. Once the complete set of the symmetry elements for the analysed molecule are identified, the sets of the equivalent atoms for each symmetry operator are settled. From the sets of the equivalent atoms a subset of atoms (called unique atoms) that generate the all atoms of the molecule is determined. Using only the coordinates of the unique atoms, the optimisation of the geometry is faster.

The group of symmetry of a chemical system can be reduced to a subgroup by deformation of the molecule under the influence of an external fields (electric field for example) or because the Jahn-Teller effect. There are also cases when the geometry of the chemical system has to be checked corresponds to a real local equilibrium or transition state. The symmetry of the system has to be reduced to a subgroup of the group of symmetry. In these cases a larger set of atoms are required and the list of the unique atoms in the new symmetry group is generated starting from relation between the two groups of symmetry. The symmetry operators (7)-(10) are very useful in the generating of the geometry of the required list of atoms.

Different sets of functions (atomic orbital, spin functions, molecular orbitals or vibration coordinates) can be adapted to the symmetry of the system. The matrices that appear in the equations of the electronic and the spinorial states or of the nuclear motion become block-diagonal. Then, the calculations are done independently in each block, reducing significantly the size and the complexity of the calculations. Applying the symmetry operators $\hat{\mathbf{O}}$ from (7)-(10), that correspond to the symmetry of the system, to the functions of the basis set $\{f_\lambda\}_{\lambda=1,\omega}$, the elements of the matrices which give the transformation the set of functions $\{f_\lambda\}_{\lambda=1,\omega}$ to $\{f'_\kappa\}_{\kappa=1,\omega}$ under the symmetry operators $f'_\kappa = \sum_{\lambda=1}^{\omega} \hat{\mathbf{O}} f_\lambda = \sum_{\lambda=1}^{\omega} \mathrm{O}_{\kappa\lambda} f_\lambda$. They determine a representation Γ for the group symmetry associated to the system. The character of the symmetry operators in this representation $\chi_\Gamma(\hat{\mathbf{O}}) = \sum_{\lambda=1}^{\omega} \mathrm{O}_{\lambda\lambda}$ is calculated as the trace of the corresponding matrices $\hat{\mathbf{O}}$. The representation Γ is reducible and can be written as a direct summation $\Gamma = \sum_i a_i \Gamma_i$ of the irreducible representation Γ_i of the symmetry group. The multiplicity of each irreducible representation is given by

$$a_i = \frac{1}{h} \sum_{\hat{\mathrm{O}}} \chi_\Gamma(\hat{\mathbf{O}}) \chi^*_{\Gamma_i}(\hat{\mathbf{O}}) \tag{11}$$

where, h is the number of the symmetry operators $\hat{\mathbf{O}}$ or the size of the point symmetry group. The star designates the complex conjugate of the character χ.

For each irreducible representation Γ_i an associated projection operator can be constructed as a combination of the symmetry operators $\hat{\mathbf{O}}$

$$\hat{\mathbf{P}}^i = \frac{1}{h}\sum_{\hat{\mathbf{O}}} \chi_i^*(\hat{\mathbf{O}})\hat{\mathbf{O}} \tag{12}$$

where the coefficients are the complex conjugate characters of the operators in that irreducible representation. The symmetry-adapted functions corresponding to each irreducible representation are built as a linear combination of the initial functions over which the projection operator $\hat{\mathbf{P}}^i$ is applied.[14]

5. CONCLUSIONS

In the present article we have presented the axis-rotation formula with some of its applications to the molecular simulations. The axis-rotation formula is the natural choice to rotate an object. It avoids the difficulties in the determination of the Euler angles and the use of the Euler angles method and the mathematical complexity of the quaternion formalism. It is a very useful tool in different fields of the molecular simulations, allowing the construction and the manipulation of the atoms or fragments of systems by rotations in a natural way. Also it is useful in the production of symmetry operators, determination of the group-symmetry of a molecule and the adaptation to the molecule symmetry of the atomic and molecular orbitals and of the vibration coordinates. Future research work should focus on way to apply the axis-rotation formula to other problems. As example we will refer here to construction of a system in conditions of the imposing constraints to the distances between the chemical bonded atoms, the build of the nanotubes and to the calculation of the electronic interaction integrals from quantum chemistry, where the transformation of the local reference frame of the atoms to the standard reference frame may be avoided. Another possible application of the rotation-formula is in Molecular Dynamics simulations of rigid molecules as an alternative to the quaternion formalism. Work in this direction is in progress.

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APPENDICES

A1. THE ROTATION FORMULA

We present here the derivation of the axis-rotation formula proposed by one of us (VC) few years ago independently before to know the derivation of the same formula in reference 15. The rotation around a unit axis $\mathbf{n}=(n_1,n_2,n_3)^T$,[16] does not affect the unit vector $\mathbf{n}$ itself and the projections of an arbitrary vector $\mathbf{r}$ to $\mathbf{n}$,

$$\mathbf{nr} = \mathbf{nr}'. \tag{13}$$

Further, the norm of the rotated vector is conserved

$$\left|\mathbf{r}'\right| = \left|\mathbf{r}\right| . \tag{14}$$

The arbitrary chosen vector $\mathbf{r}$ may be decomposed on the parallel $\mathbf{r}_{\|} = \mathbf{n}\left(\mathbf{n}^{\mathrm{T}}\mathbf{r}\right)$and the perpendicular components $\mathbf{r}_{\perp} = \mathbf{r} - \mathbf{r}_{\|} = \mathbf{r} - \mathbf{n}\left(\mathbf{n}^{\mathrm{T}}\mathbf{r}\right)$ to unit vector of the rotated vector. In agreement to the relation (13), the parallel component $\mathbf{r}_{\|} = \mathbf{n}\left(\mathbf{n}^{\mathrm{T}}\mathbf{r}\right)$ of the rotated vector $\mathbf{r}$ to $\mathbf{n}$ is conserved

$$\mathbf{r}_{\|}' = \mathbf{n}\left(\mathbf{n}^{\mathrm{T}}\mathbf{r}'\right) = \mathbf{n}\left(\mathbf{n}^{\mathrm{T}}\mathbf{r}\right) = \mathbf{r}_{\|} . \tag{15}$$

Therefore, the position vector , **r’** after rotation will become

$$\mathbf{r}' = \mathbf{r}_{\perp}' + \mathbf{r}_{\|}' = \mathbf{r}_{\perp}' + \mathbf{n}\left(\mathbf{n}^{\mathrm{T}}\mathbf{r}\right). \tag{16}$$

From (13) and (14), it results that the square (or the modulus) of the perpendicular components are not changed by rotation

$$\mathbf{r}_{\perp}^2 = \mathbf{r}'^2_{\perp} = \mathbf{r}^2 \text{-} (\mathbf{n}^{\mathrm{T}}\mathbf{r})^2 . \tag{17}$$

From dot product of the perpendicular vectors $\mathbf{r}_{\perp}$ and $\mathbf{r}'_{\perp}$ and using (14) and (17) it may be obtained

$$\mathbf{r}_{\perp}\mathbf{r}'_{\perp} = \left|\mathbf{r}_{\perp}\right|\left|\mathbf{r}'_{\perp}\right| \cos\varphi = \left[\mathbf{r}^2 \text{-} (\mathbf{n}^{\mathrm{T}}\mathbf{r})^2\right]\cos\varphi . \tag{18}$$

On other hand starting from their expressions

$$\mathbf{r}_{\perp}\mathbf{r}'_{\perp} = \left[\mathbf{r}\text{-}\mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r})\right]\left[\mathbf{r}'\text{-}\mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r}')\right] = \mathbf{r}\mathbf{r}' \text{ - } (\mathbf{n}^{\mathrm{T}}\mathbf{r})^2 . \tag{19}$$

From equations (18) and (19) it results:

$$\mathbf{r}\mathbf{r}' = \mathbf{r}\cos\varphi + (\mathbf{n}^{\mathrm{T}}\mathbf{r})^2(1 - \cos\varphi) . \tag{20}$$

The outcome cross product of the perpendicular vectors $\mathbf{r}_{\perp}$ and $\mathbf{r}'_{\perp}$ is along the rotation axis $\mathbf{n}$, and using (14) and (17) it results:

$$\mathbf{r}_{\perp} \times \mathbf{r}'_{\perp} = \mathbf{n}\mathrm{r}_{\perp}^2 \sin\varphi = \mathbf{n}\left[\mathbf{r}^2 \text{ - } (\mathbf{n}^{\mathrm{T}}\mathbf{r})^2\right]\sin\varphi . \tag{21}$$

On other hand, starting from their expressions it can be obtained:

$$\mathbf{r}_{\perp} \times \mathbf{r}'_{\perp} = \left[\mathbf{r}\text{-}\mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r})\right] \times \left[\mathbf{r}'\text{-}\mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r}')\right] = \mathbf{r} \times \mathbf{r}' \text{ - } (\mathbf{n}^{\mathrm{T}}\mathbf{r})\mathbf{n} \times \mathbf{r}' - (\mathbf{n}^{\mathrm{T}}\mathbf{r})\mathbf{r} \times \mathbf{n} . \tag{22}$$

Appling a cross product of $\mathbf{r}$ to the right of the equality of last expressions (21) and (22) and using the properties of double cross product $(\mathbf{a} \times \mathbf{b}) \times \mathbf{c} = \mathbf{b}(\mathbf{ac}) - \mathbf{a}(\mathbf{bc})$, after some algebraic manipulations it results the relation

$$\left[\mathbf{r}^2 \text{ - } (\mathbf{n}^{\mathrm{T}}\mathbf{r})^2\right]\left[\mathbf{r}'\text{-}\mathbf{r}\cos\varphi - \mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r})(1 - \cos\varphi)\right] = \left[\mathbf{r}^2 \text{ - } (\mathbf{n}^{\mathrm{T}}\mathbf{r})^2\right]\mathbf{n} \times \mathbf{r}\sin\varphi , \tag{23}$$

with two solutions:

$$\mathbf{r}^2 \text{ - } (\mathbf{n}^{\mathrm{T}}\mathbf{r})^2 = 0 , \tag{24}$$

that corresponds to the cases when the vector $\mathbf{r}$ is parallel or anti-parallel to **n**, and

$$\mathbf{r}' = \mathbf{r}\cos\varphi + \mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r})(1-\cos\varphi) + \mathbf{n}\times\mathbf{r}\sin\varphi . \tag{25}$$

The relation (25) represents the formula of the rotation around an axis with an angle $\varphi \in [0,\pi]$. The domain of values is restricted by the definition of dot and cross product of two vectors but may be extended to □ because two or more successive rotations of angles in $[0,\pi]$ can be applied around the same axis. The case described by equation (24) is contained in the relation (25). Therefore, the relation (25) is the general formula for the rotation with any angle $\varphi \in$ □ around any unit axis $\mathbf{n}$ without special cases of singularities.

A2. THE ANGULAR VELOCITY

An infinitesimal displacement $\mathrm{d}\boldsymbol{\rho}=\mathbf{v}\mathrm{dt}$ can be decomposed in an infinitesimal translation $\mathrm{d}\boldsymbol{\rho}_0=\mathbf{v}_0\mathrm{dt}$ and an infinitesimal rotation $\mathrm{d}\boldsymbol{\rho}=\mathbf{v}_{\mathrm{rot}}\mathrm{dt}$ around an unit axis $\mathbf{n}$ that is going through the point described by $\boldsymbol{\rho}_0$ with an angular velocity $\boldsymbol{\omega}=\omega\mathbf{n}$ that has the same direction as $\mathbf{n}$. The modulus $\omega=|\boldsymbol{\omega}|$ gives the rotation angle $\mathrm{d}\varphi=\omega\mathrm{dt}$.

Using the rotation formula (1) and considering the instantaneous rotation, produced around $\mathbf{n}=\boldsymbol{\omega}/\omega$ with a very small rotation angle $\Delta\varphi\to 0$, in very short time $\Delta t\to 0$, we obtain

$$\begin{aligned}
\mathbf{v}_{\mathrm{rot}} &= \dot{\mathbf{r}} = \lim_{\Delta\mathrm{t}\to 0}\frac{\mathbf{r}(\mathrm{t}+\Delta\mathrm{t})\text{-}\mathbf{r}(\mathrm{t})}{\Delta\mathrm{t}} \\
&= \lim_{\Delta\mathrm{t}\to 0}\frac{\Delta\varphi}{\Delta\mathrm{t}}\lim_{\Delta\varphi\to 0}\frac{\mathbf{r}(\Delta\varphi)\text{-}\mathbf{r}(0)}{\Delta\varphi} \\
&= \omega\lim_{\Delta\varphi\to 0}\frac{(\text{-}\mathbf{r}+\mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r}))(1-\cos\varphi)+\mathbf{n}\times\mathbf{r}\sin\varphi}{\Delta\varphi} \\
&= \omega\left(\left[\text{-}\mathbf{r}+\mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{r})\right]\lim_{\Delta\varphi\to 0}\frac{(1-\cos\varphi)}{\Delta\varphi}+\mathbf{n}\times\mathbf{r}\lim_{\Delta\varphi\to 0}\frac{\sin\varphi}{\Delta\varphi}\right) \\
&= \omega\,\mathbf{n}\times\mathbf{r} = \boldsymbol{\omega}\times\mathbf{r}
\end{aligned} \tag{26}$$

that is well known formula of rotation of any vector

$$\mathbf{v}_{\mathrm{rot}} = \dot{\mathbf{r}} = \boldsymbol{\omega}\times\mathbf{r} \tag{27}$$

A3. SOLVING THE ROTATION

Let us consider two coordinate reference frames F and F' described by the unit vectors $\{\mathbf{f}_i\}_{i=1,3}$ and $\{\mathbf{f}'_i\}_{i=1,3}$ and that the unit vectors $\{\mathbf{f}'_i\}_{i=1,3}$ are obtained by an axis-rotation with the associated matrix $\mathbf{R}$ of the elements $R_{ij}=\mathbf{f}_i\mathbf{f}'_j$.[17] The axis $\mathbf{n}$ and the angle α that correspond to rotation of the frame F to F' may be determined considering the relation (25):

$$\mathbf{f}'_j = \mathbf{f}_j\cos\alpha + \mathbf{n}(\mathbf{n}^{\mathrm{T}}\mathbf{f}_j)(1\text{-}\cos\alpha)+\mathbf{n}\times\mathbf{f}_j\sin\alpha) \tag{28}$$

From the dot product of the relation (28) with $\mathbf{f}_i$ and considering the relation the $\mathbf{f}_i(\mathbf{n}\times\mathbf{f}_j)=\mathbf{n}(\mathbf{f}_j\times\mathbf{f}_i)=\mathbf{n}\mathbf{f}_k=\mathrm{n}_\mathrm{k}$ next component in a cyclic-periodic ordering of the indices, the elements of matrix $\mathbf{R}$ are obtained as

$$R_{ij}=\mathbf{f}_i\mathbf{f'}_j=\delta_{ij}\cos\alpha+\mathrm{n}_i\mathrm{n}_j(1\text{-}\cos\alpha)\text{+}\mathrm{n}_k\sin\alpha\,. \tag{29}$$

The trace of the matrix gives the cosine of the rotational angle

$$\cos\alpha=\frac{1}{2}\left(\sum_{i=1}^{3}R_{ii}-1\right). \tag{30}$$

The difference of the extra-diagonal elements gives

$$\mathrm{n}_\mathrm{k}\sin\alpha=\frac{1}{2}\left(R_{ij}-R_{ji}\right) \tag{31}$$

therefore, the rotation axis is determined until $\sin\alpha$. It can be normalized but its direction is not defined since equation (31) has two solutions: $\mathbf{n}\sin\alpha$ and $(\mathbf{-n})\sin(-\alpha)$.

The components of $\mathbf{n}$ are not defined for a symmetric matrix $\mathbf{R}^\mathrm{T}=\mathbf{R}$ (that corresponds to $\mathbf{f}_i\mathbf{f'}_j=\mathbf{f}_j\mathbf{f'}_i$), when $\sin\alpha=0$ ($\alpha=0$ or π). In this case $\mathbf{f'}_j=\pm\mathbf{f}_j\cos\alpha+\mathbf{n}(\mathbf{n}^\mathrm{T}\mathbf{f}_j)(1\pm1)$, where the signs “+” and “–“ correspond to $\alpha=0$ and $\alpha=\pi$, respectively.
The case $\alpha=0$ corresponds to $\mathbf{f'}_j=\mathbf{f}_j$, which means that no rotation is performed. The other case $\alpha=\pi$ corresponds to $\mathbf{f'}_j=-\mathbf{f}_j+2\mathbf{n}(\mathbf{n}^\mathrm{T}\mathbf{f}_j)$ and the elements of the rotation matrix are $\mathbf{f}_i\mathbf{f'}_j=-\delta_{ij}+2\mathrm{n}_i\mathrm{n}_j$, where δ_{ij} is the Kroneker symbol. Choosing a component $\mathrm{n}_k=\sqrt{(1+\mathbf{f}_k\mathbf{f'}_k)/2}$ the others are $\mathrm{n}_i=\sqrt{(\mathbf{f}_k\mathbf{f'}_k)/(2\mathrm{n}_k)}$. To avoid the case $\mathrm{n}_k=0$ the k-th component has to correspond to the maximum diagonal element $R_{kk}=\mathbf{f}_k\mathbf{f'}_k$.

The components of an arbitrary vector $\mathbf{r}=\left(\mathrm{r}_1,\mathrm{r}_2,\mathrm{r}_3\right)^\mathrm{T}=\sum_{k=1}^{3}\mathrm{r}_k\mathbf{f}_k$ expressed in the basis in F, become $\mathbf{r}=\left(\mathrm{r}_1^{'},\mathrm{r}_2^{'},\mathrm{r}_3^{'}\right)^\mathrm{T}=\sum_{k=1}^{3}\mathrm{r'}_k\mathbf{f'}_k$ in the new basis set in F’. The two sets of components are related by $\mathrm{r}_k=\sum_{i=1}^{3}R_{ki}\mathrm{r'}_k$. By inversion and using the property of orthogonality of the rotation $\mathbf{R}^{-1}=\mathbf{R}^T$ the components of the position vector $\mathbf{r}$ in the basis F’ become

$$\mathrm{r'}_k=\sum_{i=1}^{3}R_{ik}\mathrm{r}_k \tag{32}$$

This result is something expected because a vector is not affected by the transformation of the basis set and its coordinates have to be obtained by the inverse rotation.

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