

# Rotation Minimizing Frames and their Application to the Visualization of Chemical Reactions

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## Abstract

*We apply techniques from Computer Aided Design of spatial curves to generate the trajectories of molecules involved in a chemical reaction. The main point is the use of Rotation Minimizing Frames along the trajectories, defined as Bézier curves, to visualize the motion of the molecule minimizing the twist.*

## 1 Introduction

Computer tools can be used to visualize many different things, from real objects to physical or chemical processes. Over the past few decades the technology available for such a purpose has increased significantly as well as the possibilities of its use.

Visualizations and modelling can be very useful for educational purposes, for example in the realm of Chemistry where it is often difficult to visualize atoms, molecules, reactions, etc. To acquire the skill of thinking in 3D is not an easy task for a undergraduate student. A way to gain this skill is thanks to live demonstrations which enhance the learning of concepts.

In particular, using these tools for exploring some aspects of the process taking place in a simple chemical reaction is our main concern in this work. This proposal is predominantly being used for teaching. Throughout this paper, we analyze an example of a chemical reaction in three dimensional space where two reactants interchange an atom and are transformed into two products.

A first scenario for the visualization of a reaction of this type would be to bring the reactants into the position in which the reaction occurs in a linear and uniform way, and after the reaction they separate in the same manner. This situation is, nevertheless, unrealistic since it requires both reactants, both products and the point of the reaction to be aligned. Moreover, its visualization is very unsatisfactory.

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A second and more realistic scenario would be to allow the initial and final positions of the reactants to be chosen freely. In this situation we use Bézier curves for defining the trajectories of the reactants and the products of the reaction.

Bézier curves are parametric curves that are often used in computer graphics and related fields ([5, 4, 7, 9]). Due to their nice properties, they are used in the modelling of smooth curves that can be scaled indefinitely. The curve is contained in the convex hull of its control points, which is a set of points that can be used to manipulate the curve. Thus, translations and rotations can be applied on the curve by applying them to its control points.

There is, however, a problem here too. While the movement of each molecule describes a Bézier curve towards and from the point of reaction, the molecules should also rotate on themselves to be perfectly placed in front of one another at the moment of the reaction.

A first attempt to solve this problem would be to use a reference frame intrinsic to the curve, the Frenet frame, to make the molecule rotate in space as if it was linked to that reference frame. Of course, the movement of the molecule is computed thanks to isometries of the space. The problem with this solution is that, as it is pointed out in [8], in many occasions, the Frenet frame of the curve presents exaggerated rotations and sudden orientation changes.

There is a second option: use what is called a “rotation minimizing frame” (RMF) or “parallel transport frame”. This is a concept that has recently attracted attention in the field of computer curve design, see for example [3] and [8]. Due to its minimal twist, the rotation minimizing frame is widely used in computer graphics. For example, in paper [10], some real life objects are designed using ruled surfaces from a spine curve and a rotation minimizing vector. A RMF is a frame that is associated with a curve and moves along its trajectory, very much like the Frenet frame, but reduces the nasty rotations.

The main goal of this paper is to show how the concept of rotation minimizing frames has been successfully applied to visualize simple chemical reactions in a natural way.

A Mathematica file can be downloaded from the web page of one of the authors ([www.uv.es/monterde/RMF-chemical-reaction.cdf](http://www.uv.es/monterde/RMF-chemical-reaction.cdf)) where it can be seen a model for the visualization of the chemical reaction we have used as a prototypical example. The extension of the Mathematica file (cdf) means Computable Document Format and the free program Mathematica Player (or Mathematica v7) is needed to run the file.

## 2 A short introduction to Bézier curves

Bézier curves are polynomial curves which are very popular because of their mathematical properties that allow us to manipulate them in several manners, although no special mathematical knowledge is required, see for example [4], [9]. Given  $n + 1$  control points,  $P_0, \dots, P_n$ , the Bézier curve defined by them is a polynomial curve of degree  $n$ . The polygon obtained by joining the control points with line segments in the prescribed order is called the control polygon. Its shape reflects the “basic” shape of the Bézier curve.

A Bézier curve of degree one is just a line segment joining the two control points. One of degree two is a parabolic arc joining the first and last control points. In general, they can be defined in a recursive way using the De Casteljau’s algorithm, where the main ingredient is linear interpolation. Nevertheless, we will give the definition using Bernstein polynomials.

**Definition 1** Given a set of  $n + 1$  control points  $P_0, \dots, P_n \in \mathbb{R}^n, n = 2, 3$ , the associated Bézier curve,  $\alpha : [0, 1] \rightarrow \mathbb{R}^n$ , is defined as

$$\alpha(t) = \sum_{i=0}^n B_i^n(t)P_i,$$

where

$$B_i^n(t) = \binom{n}{i} t^i (1-t)^{n-i}, \quad \binom{n}{i} = \begin{cases} \frac{n!}{i!(n-i)!}, & \text{if } 0 \leq i \leq n, \\ 0, & \text{otherwise.} \end{cases}$$

Since the Bézier curve is uniquely determined by its control points, in some cases we denote the curve by  $\alpha = \mathcal{B}[P_0, \dots, P_n]$ .

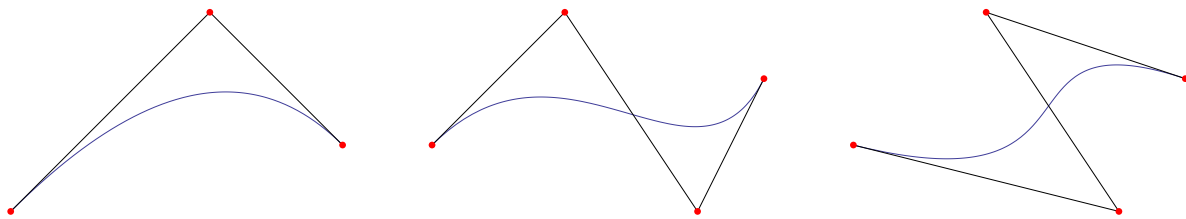


Fig. 1.- Left quadratic Bézier curve, center and right cubic Bézier curve with the same control points but different order.

## 2.1 Properties of Bézier curves

Let us recall some properties and characteristics of Bézier curves.

1. *Interpolation of the end points:* The Bézier curve passes through the end points of the control polygon  $\alpha(0) = P_0$  and  $\alpha(1) = P_n$ . Note that it's not an interpolation polynomial curve.
2. *Convex hull property:* Every point of the Bézier curve lies always inside the convex hull of its defining control points.
3. *Symmetry:* The control points,  $P_0, P_1, \dots, P_n$  and  $P_n, P_{n-1}, \dots, P_0$ , define the same Bézier curve, like a set. The only thing that changes is the direction in which we travel along the curve. In fact,

$$\alpha[P_0, P_1, \dots, P_n](t) = \alpha[P_n, P_{n-1}, \dots, P_0](1-t), \quad \text{for all } t \in \mathbb{R}.$$

**Proposition 2** The derivative of a Bézier curve  $\alpha(t)$  with control points  $P_0, \dots, P_n$  is a new Bézier curve of degree  $n - 1$  with control points  $n\Delta P_0, \dots, n\Delta P_{n-1}$ , this is,

$$\alpha'(t) = n \sum_{i=0}^{n-1} B_i^{n-1}(t)\Delta P_i,$$

where  $\Delta P_i = P_{i+1} - P_i$ , for all  $i = 0, \dots, n - 1$ .

**Remark 3** The tangent line at the initial(final) point is determined by its two first(last) control points

$$\alpha'(0) = n\Delta P_0 = n(P_1 - P_0), \quad \text{and} \quad \alpha'(1) = n\Delta P_{n-1} = n(P_n - P_{n-1}).$$

Moreover, a cubic Bézier curve is totally determined by its endpoints and their corresponding tangent vectors.

### 3 Adapted orthonormal frames

**Definition 4** Given a  $C^1$  regular space curve,  $\alpha : I \rightarrow \mathbb{R}^3$ , an adapted right-oriented orthonormal frame to  $\alpha$  is a triple of unitary vector fields along  $\alpha$ ,  $\{\vec{t}, \vec{f}, \vec{t} \wedge \vec{f}\}$ , such that

$$\vec{t} = \frac{\alpha'}{\|\alpha'\|} \quad \text{and} \quad \vec{f} \perp \vec{t}.$$

The pair  $\{\vec{f}, \vec{t} \wedge \vec{f}\}$  span the normal plane of the curve in any point of  $\alpha$ , so we only have to choose an unitary vector on that plane,  $\vec{f}$ , in order to have an adapted orthonormal frame. The classical example is the Frenet frame but this is not the only frame that can be attached to a curve.

#### 3.1 Frenet frame

We are going to use the definitions and notations from reference [2].

Let  $\alpha : I \rightarrow \mathbb{R}^3$  be an arc length parametric curve. Unless otherwise stated, the objects are of the necessary order of derivability.

The curvature function of the curve is  $\kappa(s) = \|\dot{\vec{t}}(s)\|$ . The normal vector is defined by

$$\vec{n}(s) = \frac{\dot{\vec{t}}(s)}{\|\dot{\vec{t}}(s)\|} = \frac{\dot{\vec{t}}(s)}{\kappa(s)},$$

The set  $\{\vec{t}(s), \vec{n}(s), \vec{b}(s) = \vec{t}(s) \wedge \vec{n}(s)\}$  is an adapted frame, called the Frenet frame. The vector  $\vec{b}(s)$  is called the binormal vector.

Since the Frenet frame is a basis of  $\mathbb{R}^3$ , we can express the derivatives of those vectors as a linear combination of them.

**Definition 5** Let  $\alpha$  be an arc length parametric curve with non vanishing curvature,  $\kappa(s) = \|\dot{\vec{t}}\| \neq 0$  we define the torsion function as

$$\tau(s) = -\dot{\vec{n}} \cdot \vec{b}.$$

Therefore, the Frenet formulas are an expression of the first variation of the Frenet frame

$$\begin{cases} \dot{\vec{t}}(s) &= & \kappa(s)\vec{n}(s), \\ \dot{\vec{n}}(s) &= & -\kappa(s)\vec{t}(s) & -\tau(s)\vec{b}(s), \\ \dot{\vec{b}}(s) &= & \tau(s)\vec{n}(s). \end{cases}$$

**Remark 6** We are using for the sign of the torsion the same convention than in [2]. This is the opposite sign convention from [8].

When the curve is not parameterized by arc length, the Frenet elements are calculated in the following way:

**Proposition 7** Given a regular curve,  $\alpha : I \rightarrow \mathbb{R}^3$ , the Frenet frame is

$$\vec{t} = \frac{\alpha'}{\|\alpha'\|}, \quad \vec{b} = \frac{\alpha' \wedge \alpha''}{\|\alpha' \wedge \alpha''\|}, \quad \vec{n} = \vec{b} \wedge \vec{t}, \quad (1)$$

and the curvature and torsion are the functions given, respectively, by

$$\kappa = \frac{\|\alpha' \wedge \alpha''\|}{\|\alpha'\|^3}, \quad \tau = -\frac{\det(\alpha', \alpha'', \alpha''')}{\|\alpha' \wedge \alpha''\|^2}. \quad (2)$$

**Example 8** Given the curve

$$\alpha(t) = (3t - 3t^2 + t^3, 1 - 3t^2 + 2t^3, 2t^3), \quad t \in \mathbb{R},$$

let us calculate the corresponding Frenet frame, the curvature and torsion of  $\alpha(t)$ . The curve is not parametrized by the arc length therefore we use formulae (1) and (2).

$$\begin{aligned} \vec{t} &= \frac{1}{1-2t+3t^2}(t^2 - 2t + 1, 2t^2 - 2t, 2t^2), \\ \vec{b} &= \frac{1}{1-2t+3t^2}(-2t^2, 2t^2 - 2t, -t^2 + 2t - 1), \\ \vec{n} &= \vec{b} \wedge \vec{t} = \frac{1}{1-2t+3t^2}(2t^2 - 2t, t^2 + 2t - 1, -2t^2 + 2t), \\ \kappa &= \frac{2}{3(1-2t+3t^2)^2}, \quad \tau = \frac{2}{3(1-2t+3t^2)^2}. \end{aligned}$$

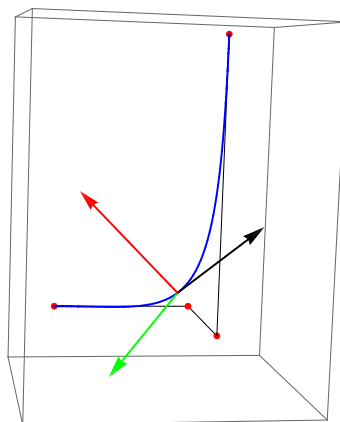


Fig. 2.- The curve with its Frenet frame and control points.

**Remark 9** The curve in Example 8 is polynomial and therefore its restriction to the interval  $[0, 1]$  is a cubic Bézier curve with control points

$$P_0 = \alpha(0) = (0, 1, 0), \quad P_1 = (1, 1, 0), \quad P_2 = (1, 0, 0), \quad P_3 = \alpha(1) = (1, 0, 2),$$

where we used Prop. 2 in order to determine the control points  $P_1$  and  $P_2$  from  $\alpha'(0) = 3(P_1 - P_0)$  and  $\alpha'(1) = 3(P_3 - P_2)$ .

### 3.2 Frenet frame at the endpoints of a Bézier curve

In order to model the motion of the molecules along Bézier curves in the following sections, we need the initial and final positions (first and last control points) and a reference frame in the final position. The Bézier curve of lower degree which can be defined with these conditions is a curve of degree 3.

We want to find a cubic Bézier curve with fixed initial and final points,  $P_0$  and  $P_3$  respectively, and with a fixed Frenet frame at the final point given by a right oriented orthonormal basis

$$\{\vec{u}_1, \vec{u}_2, \vec{u}_3\}.$$

What should the other points of control be? The solution is not unique. There are infinitely many solutions for  $P_1$  and  $P_2$ .

**Proposition 10** *Let  $P_0$  and  $P_3$  be two points in  $\mathbb{R}^3$  and  $\{\vec{u}_1, \vec{u}_2, \vec{u}_3\}$  be a right oriented orthonormal frame in  $\mathbb{R}^3$ . The cubic Bézier curve,  $\alpha : [0, 1] \rightarrow \mathbb{R}^3$  associated to the control points  $P_0, P_1, P_2, P_3$  where*

$$\begin{cases} P_2 := P_3 - \mu \vec{u}_1, & \mu \in \mathbb{R}^+ \\ P_1 := P_2 + \lambda \vec{u}_2 + \omega \vec{u}_1, & \lambda \in \mathbb{R}^+, \omega \in \mathbb{R}, \end{cases} \quad (3)$$

satisfies the following conditions:

1. *interpolates the endpoints,  $\alpha(0) = P_0$  and  $\alpha(1) = P_3$ .*
2. *its Frenet frame at the final point is given by,*

$$\left\{ \vec{t}(1) = \vec{u}_1, \vec{n}(1) = \vec{u}_2, \vec{b}(1) = \vec{u}_3 \right\}.$$

**Proof.** The first and second derivatives of the curve  $\alpha$  at its endpoint, see Prop. 2, are respectively,

$$\begin{aligned} \alpha'(1) &= 3(P_3 - P_2) = 3\mu \vec{u}_1, \\ \alpha''(1) &= 2(3(P_3 - P_2) - 3(P_2 - P_1)) = 6\mu \vec{u}_1 - 6(-\lambda \vec{u}_2 - \omega \vec{u}_1) = 6((\mu + \omega)\vec{u}_1 + \lambda \vec{u}_2) \end{aligned}$$

then

$$\vec{t}(1) = \frac{\alpha'(1)}{\|\alpha'(1)\|} = \vec{u}_1, \quad \vec{b}(1) = \frac{\alpha'(1) \wedge \alpha''(1)}{\|\alpha'(1) \wedge \alpha''(1)\|} = \frac{18\mu\lambda \vec{u}_1 \wedge \vec{u}_2}{18\mu\lambda \|\vec{u}_1 \wedge \vec{u}_2\|} = \vec{u}_3,$$

where we used that  $\{\vec{u}_1, \vec{u}_2, \vec{u}_3\}$  is a right oriented orthonormal frame in  $\mathbb{R}^3$ .

Since the Frenet frame is also a right oriented orthonormal frame, we have that

$$\vec{n}(1) = \vec{b}(1) \wedge \vec{t}(1) = \vec{u}_3 \wedge \vec{u}_1 = \vec{u}_2.$$

■

**Remark 11** *In fact, all possible solutions are given in the statement of Prop. 10. Parameters  $\mu, \lambda$  and  $\omega$  can be useful to adjust the shape of the curve as we will see later.*

We will also use the previous result with different initial conditions because sometimes we will need to build a curve when the given Frenet frame is at  $t = 0$ , not at  $t = 1$  as in Prop. 10. In this case we will compute the curve as in the statement, this is, as if the given Frenet frame was at  $t = 1$ , but afterwards we travel along the curve reversing the direction.

### 3.3 Rotation minimizing frames

Now we will define the notion of rotation minimizing frames, also known as relatively parallel adapted frames or Bishop frames (see [1]), we will explore some of their properties and compare them to Frenet frames. The main idea here is to avoid/limitate the unnecessary rotations of the adapted frame in the normal plane to the curve.

**Definition 12** (See [10] or [6]) *Given a regular curve  $\alpha : [0, 1] \rightarrow \mathbb{R}^3$  a right-oriented orthonormal adapted frame,  $\{\vec{t}, \vec{f}, \vec{t} \wedge \vec{f}\}$  is a rotation-minimizing frame (in short RMF) if  $\vec{f}'$  is parallel to  $\vec{t}$ . Here, the vector  $\vec{f}$  is called the reference vector of the RMF.*

**Remark 13** *Note that the reference vector is a vector field along the curve,  $\vec{f} : I \rightarrow \mathbb{R}^3$ , such that*

$$\left. \begin{array}{l} (a) \quad \vec{f}'(u) - \psi(u)\vec{t}(u) = 0 \\ (b) \quad \vec{f}(u) \cdot \vec{t}(u) = 0 \end{array} \right\} \quad (4)$$

for some function  $\psi$ .

**Remark 14** *The RMF is determined only by the geometry of the curve and it's independent of any particular parameterization of the curve.*

The condition  $\vec{f}'$  parallel to  $\vec{t}$  implies the vanishing of the projection onto the plane orthogonal to  $\vec{t}$  of the derivative of  $\vec{f}$ , or in other words, that the vector field  $\vec{f}$ , along  $\alpha$ , moves in a parallel way in the sense of parallel transport (see [1]). Therefore, the only spatial rotation that  $\vec{f}$  has is the one coming from the curve  $\alpha$ .

### 3.4 Integration of equations of the RMF

We start with the Frenet frame  $\{\vec{t}, \vec{n}, \vec{b} = \vec{t} \wedge \vec{n}\}$  of an arc length parametrized curve  $\alpha$  and then we calculate the RMF of this curve.

It is clear that the normal plane to the curve, at each point, is generated by vectors  $\vec{n}$  and  $\vec{b}$ , thus, it is natural to look for a reference vector  $\vec{f}$  of the form

$$\vec{f}(s) = A(s)\vec{n}(s) + B(s)\vec{b}(s)$$

for some functions  $A(s)$  and  $B(s)$ . Hence, it is clear that in this way Eq. (4-(b)) is satisfied. Since  $\|\vec{f}(s)\| = 1$ , we can assume that  $A(s) = \cos(\psi(s))$  and  $B(s) = \sin(\psi(s))$ . Therefore, differentiating  $\vec{f}(s)$  and using Frenet formulas, we get

$$\begin{aligned} \dot{\vec{f}} &= (\cos \psi \vec{n} + \sin \psi \vec{b})' = -\sin \psi \dot{\psi} \vec{n} + \cos \psi \dot{\vec{n}} + \cos \psi \dot{\psi} \vec{b} + \sin \psi \dot{\vec{b}} \\ &= (-\kappa \cos \psi) \vec{t} + (-\dot{\psi} + \tau) \sin \psi \vec{n} + (\dot{\psi} - \tau) \cos \psi \vec{b}. \end{aligned}$$

From Eq. (4-(a)), we have  $\dot{\vec{f}} = \dot{\psi} \cdot \vec{t}$ , so we have that  $\dot{\vec{f}} \cdot \vec{n} = 0 = \dot{\vec{f}} \cdot \vec{b}$ , or equivalently,

$$(-\dot{\psi} + \tau) \sin \psi = 0, \quad \text{and} \quad (\dot{\psi} - \tau) \cos \psi = 0.$$

Since the trigonometric functions, sin and cos, cannot be zero simultaneously, then  $\dot{\psi} = \tau$  and

$$\psi(t) = \int_{t_0}^t \tau(s) ds = \int_{t_0}^t \tau(v) \|\alpha'(v)\| dv, \quad (5)$$

since  $ds = \|\alpha'(v)\| dv$ .

**Example 15** We illustrate the process to calculate a rotation minimizing frame with the cubic curve of Example 8,

$$\alpha(t) = (3t - 3t^2 + t^3, 1 - 3t^2 + 2t^3, 2t^3), \quad t \in [0, 1].$$

We have shown that the velocity and the torsion are

$$\|\alpha'(t)\| = 3(1 - 2t + 3t^2), \quad \tau(t) = \frac{2}{3(1 - 2t + 3t^2)^2}.$$

Therefore, the angle defining the RMF of  $\alpha(t)$  is

$$\psi(t) = \int_0^t \tau(v) \|\alpha'(v)\| dv = \int_0^t \frac{2}{1 - 2v + 3v^2} dv = \sqrt{2} \left( \arctan\left(\frac{3t - 1}{\sqrt{2}}\right) + \arctan\left(\frac{1}{\sqrt{2}}\right) \right).$$

So, the RMF of  $\alpha$  is  $\{\vec{t}(t), \vec{f}(t), \vec{t}(t) \wedge \vec{f}(t)\}$  where

$$\begin{aligned} \vec{f}(t) &= \cos(\psi(t))\vec{n}(t) + \sin(\psi(t))\vec{b}(t) \\ \vec{t}(t) \wedge \vec{f}(t) &= \cos(\psi(t))\vec{b}(t) - \sin(\psi(t))\vec{n}(t). \end{aligned}$$

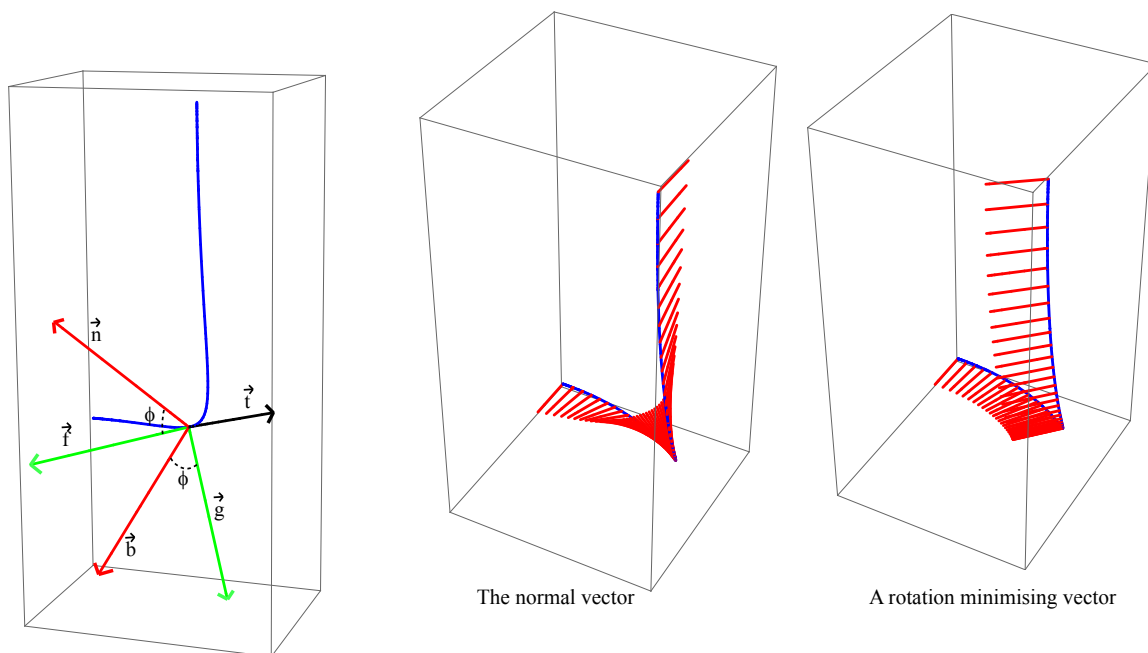


Fig. 3.- The curve  $\alpha(t)$  and its Frenet frame and RMF (left), the curve and the normal vector field (center) and a rotation minimizing vector field (right).

We can see in Fig. 3 the Frenet frame (shown in red) compared to the rotation minimizing frame (shown in green) at a single point. The angle between the two frames is  $\phi$ . Moreover, we can see that the normal vector is rotating more than a rotation minimizing vector.



## 4 The problem

Now we address the problem of modelling and visualizing, in a realistic way, the movement of two separated molecules which are approaching to each other, then they react chemically, and separate afterwards.

To begin with, let us suppose that all the reactions we are going to visualize involve two molecules, each of one having more than two atoms.

In each reaction there is one atom that moves from one molecule to the other. We will call this atom **the transfer atom**. Before the reaction, this atom is joined to the first molecule by a bond. At the reaction time, another bond is formed between the atom and the second molecule. The reaction ends when the bond with the first molecule is subsequently broken and the transfer atom is only joined to the second molecule.

The atom of the first molecule, having a bond with the transfer atom will be called **the principal atom of the first molecule**. The atom of the second molecule which captures the transfer atom and forms a bond with it, will be called **the principal atom of the second molecule**. On these two principal atoms will be set the origin for each one of the reference frames of the respective molecules.

The vector defined by the relative positions of the transfer atom and the principal atom on the second molecule, that is the vector settled by the bond formed between these two atoms, will be called **the reaction vector**.

We can construct a reference frame for each one of the molecules in the instant of the reaction. For the first molecule we will initially consider the reaction vector, say  $\vec{u}$ , and the vector defined by the bond between its principal atom and the transfer atom, say  $\vec{v}$ . From  $\{\vec{u}, \vec{v}\}$  we can construct another two vectors, say  $\vec{x}$  and  $\vec{y}$  such that  $\vec{x} \cdot \vec{y} = 0$ ,  $\|\vec{x}\| = \|\vec{y}\| = 1$ , and  $\text{Span}(\{\vec{u}, \vec{v}\}) = \text{Span}(\{\vec{x}, \vec{y}\})$ . The third vector of the reference frame is defined as the vector product of  $\vec{x}$  and  $\vec{y}$ :  $\vec{z} = \vec{x} \wedge \vec{y}$ . Thus  $\{\vec{x}, \vec{y}, \vec{z}\}$  is a right oriented orthonormal basis.

For the second molecule we will initially consider the reaction vector and the vector defined by another bond in this molecule to which the principal atom is also joined. We then repeat the process of forming a right oriented orthonormal basis that generates the same vector subspace and we complete this basis with the vector product of the two initial vectors.

Therefore we have, in this way, a reference frame attached to each molecule. When a translation and/or rotation is applied to the reference frame, this same rigid movement is applied to the whole molecule. This is to say that the distances and angles between the atoms in the molecule remain the same.

To get a better understanding of what we are doing we will use as an example a classical chemical reaction of the kind “acid–base reaction”.

**Example 16** *The reactants are Hydrogen Sulphide ( $H_2S$ ) which is an acid and Ammonia ( $NH_3$ ) which is a base. The product of the reaction,  $NH_4 + SH^-$  is called “Ammonium Hydrogen Sulphide”.*

Let  $R_k$  denote the coordinates of atom  $k$  in the position of the reaction and suppose that

$$\begin{cases} R_1 = (2.89, 0., 0.), \\ R_2 = (3.83, 0.79, 0.), \\ R_3 = (4.79, 0., 0.), \end{cases} \quad \begin{cases} R_4 = (5.84, 0., 0.), \\ R_5 = (6.23, -0.48, -0.83), \\ R_6 = (6.23, -0.48, 0.83), \\ R_7 = (6.23, 1., 0.). \end{cases} \quad (6)$$

**Remark 17** At the reaction time the seven atoms form a molecule as a whole. Internal distances and angles between atoms are fixed, but the position of this molecule at the space is arbitrary. Positions given by (6) have been chosen to obtain later a simple frame at the reaction point. For example, the axis defined by the bond between atoms 3 and 4 is the  $x$ -axis. The choice of the position of atoms 2, 3 and 4, fixes the position of the rest.

The molecule on the left approaches the other; the bond between atoms 2 and 3 is broken and atom 3 bonds with atom 4 of the molecule on the right.

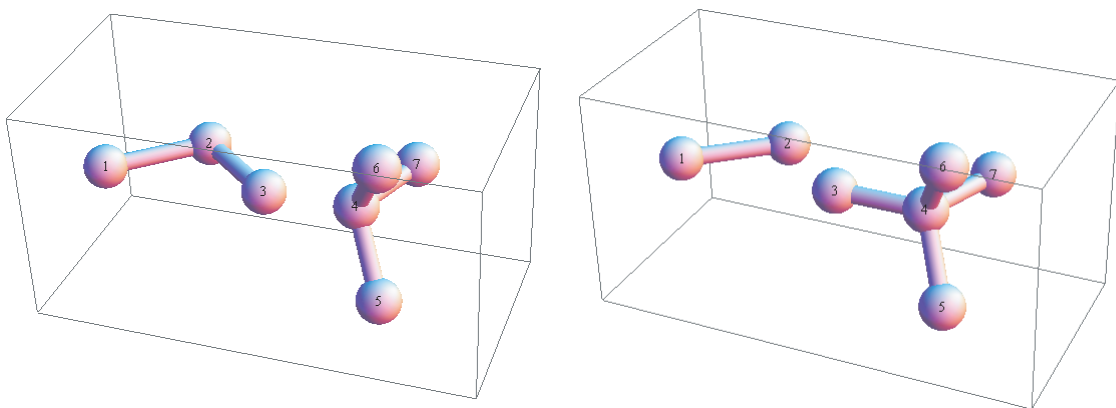


Fig. 4.-Left, Hydrogen Sulphide(left) and Ammonia(right) before the reaction. Right the product of the reaction.

In this example, the transfer atom is atom number 3. The principal atom of the first molecule is atom number 2 and the principal atom of the second molecule is atom number 4. The reaction vector is the vector joining  $R_3$  and  $R_4$ . The reference frames for the two molecules will be constructed later on.

#### 4.1 The solution when only one molecule moves

We will work only with the movement from the initial position to the position just before the reaction. In Fig. 4 we can see that there is a bond on the moving molecule that binds atoms 2 and 3, and this bond will disappear upon reaction with the other molecule. It is atom 3 that will be trapped by molecule 2.

We will define a Bézier curve on which atom 2 will be moving, from its initial position towards its position at the instant of the reaction. As determining as it is the position at the instant of the reaction,

we will construct a reference frame on the molecule that is moving to this position before the reaction. The frame is defined by the three following vectors:

1. The reaction vector, the vector defined by the bond to be formed. In the example, this vector is defined by the positions of atoms 3 and 4 at the instant of the reaction:

$$\vec{u}_1 = \frac{R_4 - R_3}{\|R_4 - R_3\|} = \frac{(5.84, 0., 0.) - (4.79, 0., 0.)}{\|(5.84, 0., 0.) - (4.79, 0., 0.)\|} = (1, 0, 0).$$

2. To define  $\vec{u}_3$ , first we select a different bond from the first molecule, in the example we choose the bond between 2 and 3 and we call it  $\vec{v}$ . The vector  $\vec{u}_3$  is now the normalization of the vector product  $\vec{u}_1 \wedge \vec{v}$ . In the example,  $\vec{v} = R_3 - R_2 = (4.79, 0., 0.) - (3.83, 0.79, 0.) = (0.96, -0.79, 0.)$ , and

$$\vec{u}_3 = \frac{\vec{u}_1 \wedge \vec{v}}{\|\vec{u}_1 \wedge \vec{v}\|} = \frac{(1, 0, 0) \wedge (0.96, -0.79, 0.)}{0.79} = (0, 0, -1).$$

3. Finally, the third vector,  $\vec{u}_2 = \vec{u}_3 \wedge \vec{u}_1$ . In the example,  $\vec{u}_2 = (0, 0, -1) \wedge (1, 0, 0) = (0, -1, 0)$ .

Thus, the family of vectors  $\{\vec{u}_1 = (1, 0, 0), \vec{u}_2 = (0, -1, 0), \vec{u}_3 = (0, 0, -1)\}$  is a positively oriented orthonormal basis.

We now need to look for the cubic Bézier curve with the following conditions:

1. Interpolates the endpoints: the initial point ( $t = 0$ ) is the position of atom 2 in the initial instant,  $I_2$  and the final point ( $t = 1$ ) is the position of atom 2 in the instant before the reaction,  $R_2$ .
2. The Frenet frame at the final point is the frame that we have constructed

$$\{\vec{t}(1) = \vec{u}_1, \vec{n}(1) = \vec{u}_2, \vec{b}(1) = \vec{u}_3\}.$$

The Bézier curve of lower degree that can be defined with these conditions (see Prop. 10) is a curve of degree 3 that has control points:

1.  $P_0 = I_2$  and  $P_3 = R_2$ , because interpolates position of atom 2.
2.  $P_2 = P_3 - \mu \vec{u}_1 = R_2 - \mu \frac{R_4 - R_3}{\|R_4 - R_3\|}$ .
3. For  $P_1$  we will apply Eq. (3) with  $\lambda = 1$  and  $\omega = 0$ ,

$$\begin{aligned} P_1 &= P_2 + \vec{u}_2 = R_2 - \mu \frac{R_4 - R_3}{\|R_4 - R_3\|} + \frac{\vec{u}_1 \wedge \vec{v}}{\|\vec{u}_1 \wedge \vec{v}\|} \wedge \vec{u}_1 \\ &= R_2 - \mu \frac{R_4 - R_3}{\|R_4 - R_3\|} + \frac{(R_4 - R_3) \wedge (R_3 - R_2)}{\|(R_4 - R_3) \wedge (R_3 - R_2)\|} \wedge \frac{R_4 - R_3}{\|R_4 - R_3\|}. \end{aligned}$$

**Remark 18** In order to construct the associated Bézier curve, we only need the initial position of atom 2,  $I_2$ , and the reaction position of atoms 3, 4 and 2,  $R_3$ ,  $R_4$  and  $R_2$ . This is because the other initial positions will be computed from the Bézier curve and the rotation minimizing frame.

The parameters  $\mu$  and  $\lambda$  are used to manipulate the curve. In our example, if  $\mu = 1$  the trajectory of the molecule would not approach the point of reaction in a linear way. We have set  $\mu = 3$ ,  $\lambda = 1$  and  $\omega = 0$ . By doing so, the molecule approaches the reaction point almost in a straight line. This resembles more accurately what occurs in reality, when molecules have a reaction they are attracted to each other and as they begin to get closer the attraction forces them together in the quickest way possible - that is, linearly. With those values of the parameters we are able to capture this linear movement close to the point of the reaction, thus making our visualization more realistic.

In the example, the value of the initial position  $I_2 = (-2, -2, 3)$ , reaction positions  $R_2, R_3, R_4$  given in (6) and values  $\mu = 3, \lambda = 1, \omega = 0$  determine the control points

$$P_0 = (-2, -2, 3), P_1 = (0.83, -0.21, 0.), P_2 = (0.83, 0.79, 0.), P_3 = (3.83, 0.79, 0.),$$

and the cubic Bézier curve

$$\alpha(t) = (-2. + 8.49 t - 8.49 t^2 + 5.83 t^3, -2. + 5.37 t - 2.37 t^2 - 0.21 t^3, 3. - 9. t + 9. t^2 - 3. t^3). \quad (7)$$

## 4.2 Reference system that minimizes the rotation

The frame is needed because the molecule has to move rigidly. Placing the Frenet frame at the final point of the constructed trajectory we are sure that final position of the molecule is correct.

We have already calculated the Bézier curve, so this is a good point to start. From here we can move on to calculate the RMF. Let us see what happens in the example which we are working with:

First we must calculate the torsion, see Eq. (2), of the curve given in (7),

$$\tau(t) = -\frac{972.0}{5510.88 - 31891.3 t + 92694.1 t^2 - 101319.0 t^3 + 37921.0 t^4}.$$

We can then move on to calculate the function  $\psi(t)$  defined by Eq. (5). However the function to integrate in our example is

$$\tau(t) \|\alpha'(t)\| = -\frac{0.50\sqrt{0.47 - 1.71 t + 2.81 t^2 - 2.36 t^3 + t^4}}{0.15 - 0.84 t + 2.44 t^2 - 2.67 t^3 + t^4}.$$

The angle function  $\psi(t)$  does not have an integral expressible by comprehensive known functions, as was the case in Example 15. It can only be calculated numerically. As the function  $\psi(t)$  cannot explicitly be calculated, neither can the rotation minimizing frame.

Notice that, since we have prescribed the Frenet frame at  $t = 1$  but not at  $t = 0$ , then Eq. (5) can be developed as follows:

$$\psi(t) = \int_{t_0}^t \tau(s) ds = \psi_0 + \int_0^t \tau(s) ds.$$

We can compute  $\psi_0$  by noticing that  $\psi(1) = 0$ . Indeed,

$$0 = \psi(1) = \psi_0 + \int_0^1 \tau(s) ds \rightarrow \psi_0 = -\int_0^1 \tau(s) ds,$$

and the angle defining the RMF is

$$\psi(t) = -\int_0^1 \tau(s) ds + \int_0^t \tau(s) ds = -\int_t^1 \tau(s) ds.$$

**Remark 19** *A solution that was initially considered was to set the Frenet frame at the starting and final points. This requires the use of a curve of degree 6. The problem here is that making the molecule to move along the curve and rotate according to the Frenet frame of the curve, there are instances where the molecule rotates too much.*

*To avoid this problem, it is necessary to use another frame associated with the curve, one that minimizes the rotation of the normal plane around the unitary tangent vector to the curve. However, for the moment it is not known how to calculate this frame if it is fixed to the Frenet frame at both the initial and final points.*

Now we are going to compute the expression of the RMF in terms of the Frenet frame. According to Section 3.4, the vector field  $\vec{u} = \cos \psi \vec{n} + \sin \psi \vec{b}$  is a reference vector of the RMF and, according to Definition 12,  $\{\vec{t}, \vec{u}, \vec{v} := \vec{t} \wedge \vec{u}\}$  is a RMF adapted to the curve. An easy computation shows that  $\vec{v} = -\sin \psi \vec{n} + \cos \psi \vec{b}$ .

Once we have both the curve,  $\alpha$  and the rotation minimizing frame we have to compute the position of the molecule at the instant  $t \in [0, 1]$ . This can be done as follows: For each  $t$ , we have an affine frame defined by an origin point  $\alpha(t)$  and a basis  $\{\vec{t}(t), \vec{u}(t), \vec{v}(t)\}$ . Since the positions of the atoms at the reaction time, this is for  $t = 1$ , are known, all we have to do is to transport each atom from  $t = 1$  to another  $t \in [0, 1[$  using the rigid motion defined by the corresponding affine frames. The rigid motion is the composition between the translation sending  $\alpha(1)$  into  $\alpha(t)$  and the spatial rotation transforming  $\{\vec{t}(1), \vec{u}(1), \vec{v}(1)\}$  into  $\{\vec{t}(t), \vec{u}(t), \vec{v}(t)\}$ .

Let  $T_t$  be the matrix defined by the right oriented orthonormal basis,  $\{\vec{t}(t), \vec{u}(t), \vec{v}(t)\}$ , or equivalently, the spatial rotation transforming the canonical basis into  $\{\vec{t}(t), \vec{u}(t), \vec{v}(t)\}$ . Thus, the spatial rotation transforming  $\{\vec{t}(1), \vec{u}(1), \vec{v}(1)\}$  into  $\{\vec{t}(t), \vec{u}(t), \vec{v}(t)\}$  is the composition  $T_t \circ T_1^{-1}$ .

Therefore, the position of the  $k$ -th atom in the prototypical example we are working with, is

$$\alpha(t) + T_t (T_1^{-1}(R_k - R_7)),$$

where  $T_t$  denotes the matrix formed by the three vectors of the RMF at the instant  $t \in [0, 1]$ , and  $T_1^{-1}$  is the inverse of this matrix when  $t = 1$ . It is easy to check that for  $t = 1$ , the final position of atom  $k$  in the molecule is obtained. Indeed,

$$\alpha(1) + T_1 (T_1^{-1}(R_k - R_7)) = R_7 + R_k - R_7 = R_k.$$

### 4.3 The solution when both molecules move

We have derived a solution to our problem when one molecule (Hydrogen Sulphide) moves and the other one (Ammonia) remains still, see Fig. 5. Now, we will look for a solution when both molecules move towards each other, then they react and move away.

In this case, it is necessary to construct four Bézier curves:

1.  $\alpha_A^1$  - from the initial position of A to the position of A at the instant of the reaction.
2.  $\alpha_A^2$  - from the position of A at the instant of the reaction to the final position of A.
3.  $\alpha_B^1$  - from the initial position of B to the position of B at the instant of the reaction.

4.  $\alpha_B^2$  - from the position of B at the instant of the reaction to the final position of B.

All these curves follow atom 2 for  $\alpha_A$  and atom 4 for  $\alpha_B$ . They are constructed as in Subsection 4.1, so, we only need to specify the initial positions of the principal atoms of both molecules

$$I_2 = (-2, -2, 3), \quad I_4 = (12, 4, -3),$$

the positions at the instant of the reaction given in Eq. (6), the final positions of the principal atoms of both molecules

$$F_2 = (-2, 2, -3), \quad F_4 = (12, -4, 3),$$

and the value of the parameters  $\mu, \lambda, \omega$  of Prop. 10. For all these curves, we choose  $\mu = 3, \lambda = 1$  and  $\omega = 0$ .

The initial and final positions of the atoms 1,3,5,6 and 7 are calculated from  $I_2, I_4, F_2, F_4$  and from the positions of all the atoms at the instant of the reaction (see Remark 18).

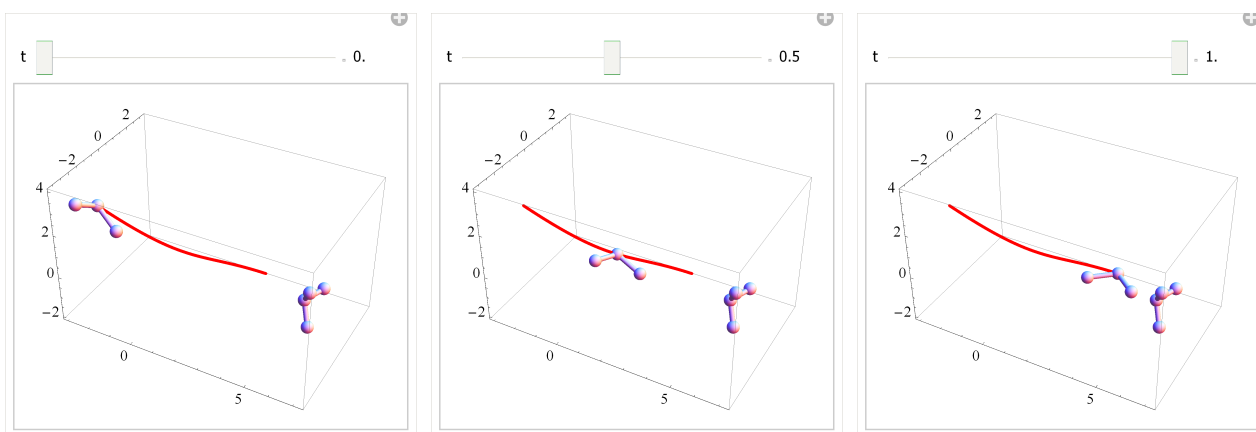


Fig. 5.- Three positions of the reactant for  $t = 0, 0.5$  and  $1$ . The Bézier curve is also shown.

### 4.3.1 The curve of the first reactant

Given that the positions at the instant of the reaction of all the atoms and the initial position of the principal atom of the first molecule are the same as those handled in Subsection 4.1, the Bézier curve  $\alpha_A^1$  is just the one given in (7),

$$\alpha_A^1(t) = (-2. + 8.49 t - 8.49 t^2 + 5.83 t^3, -2. + 5.37 t - 2.37 t^2 - 0.21 t^3, 3. - 9. t + 9. t^2 - 3. t^3),$$

with control points

$$P_0 = (-2, -2, 3), \quad P_1 = (0.83, -0.21, 0.), \quad P_2 = (0.83, 0.79, 0.), \quad P_3 = (3.83, 0.79, 0.).$$

### 4.3.2 The curve of the first product

We will now calculate the curve,  $\alpha_A^2$ , of the first molecule after the reaction. In this case the curve  $\alpha_A^2$  should start in the position at the instant of reaction of atom 2,  $R_2$ , terminating at the final position of this atom,  $F_2$ . The Frenet frame should also be fixed in the instant of the reaction. Applying Prop. 10

to a curve having  $F_2$  as its initial point and  $R_2$  as its final point, then the Frenet frame is fixed at the final point of the curve. Once the curve has been calculated we reverse its direction.

In this way, the only difference between this curve and  $\alpha_A^1$  is the initial point. If before it was  $I_2$ , now it is  $F_2$ . Thus, the control points of the curve, according to Prop. 10, are

$$P_0 = (-2, 2, -3), P_1 = (0.83, -0.21, 0.), P_2 = (0.83, 0.79, 0.), P_3 = (3.83, 0.79, 0.),$$

and the associated Bézier curve is

$$(-2. + 8.49 t - 8.49 t^2 + 5.83 t^3, 2. - 6.63 t + 9.63 t^2 - 4.21 t^3, -3. + 9. t - 9. t^2 + 3. t^3).$$

Once we have reversed the direction of the curve under the change of parameter  $t \rightarrow 1 - t$ , the control points (due to the symmetry property of Bézier curves, see Subsection 2.1) become

$$P_0 = (3.83, 0.79, 0.), P_1 = (0.83, 0.79, 0.), P_2 = (0.83, -0.21, 0.), P_3 = (-2, 2, -3),$$

and the associated Bézier curve is

$$\alpha_A^2(t) = (3.83 - 9. t + 9. t^2 - 5.83 t^3, 0.79 - 3. t^2 + 4.21 t^3, -3. t^3).$$

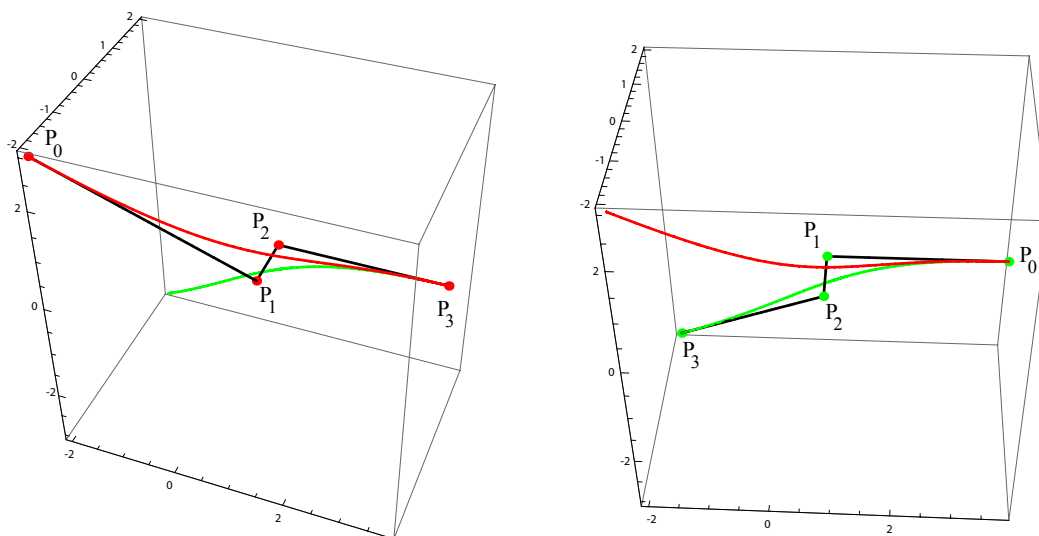


Fig. 6.- The two control polygons of the curves modelling the movement of the first molecule.

### 4.3.3 The curve of the second reactant

Now we proceed to calculate the parametric form of curve,  $\alpha_B^1$ , which describes the trajectory of the principal atom of the second molecule, namely, atom 4, from its initial position ( $I_4 = P_0$ ) to the position at the instant of the reaction ( $R_4 = P_3$ ).

In this case, we apply Prop. 10, as in Subsection 4.1, to vector  $\vec{u}_1 = \frac{R_3 - R_4}{\|R_3 - R_4\|} = (-1, 0, 0)$  and in order to define the binormal vector at the final point,  $\vec{u}_3$ , we use the vector that joins the principal atom, 5, with the atom 4,  $\vec{v} = R_4 - R_5$  and then

$$\vec{u}_3 = \frac{\vec{u}_1 \wedge \vec{v}}{\|\vec{u}_1 \wedge \vec{v}\|} = (0, 0.87, -0.50) \quad \text{and} \quad \tilde{u}_2 = \tilde{u}_3 \wedge \tilde{u}_1 = (0, 0.50, 0.87).$$

Thus, the control points for  $\mu = 3$ ,  $\lambda = 1$  and  $\omega = 0$  are

$$P_0 = (12, 4, -3), P_1 = (8.84, 0.50, 0.87), P_2 = (8.84, 0., 0.), P_3 = (5.84, 0., 0.),$$

and the associated Bézier curve:

$$\alpha_B^1(t) = (12. - 9.47t + 9.47t^2 - 6.16t^3, 4. - 10.50t + 9. t^2 - 2.50t^3, -3. + 11.60t - 14.20t^2 + 5.60t^3).$$

#### 4.3.4 The curve of the second product

We will now calculate the curve,  $\alpha_B^2$ , which describes the trajectory of the second molecule from its position in the instant of the reaction to its final position. As before, the only change, with respect to the curve of the second reactant, is that now  $P_0 = F_4$ .

Therefore, the control points of the curve, according to Prop. 10 for  $\mu = 3$ ,  $\lambda = 1$  and  $\omega = 0$ , are

$$P_0 = (12, -4, 3), P_1 = (8.84, 0.50, 0.87), P_2 = (8.84, 0., 0.), P_3 = (5.84, 0., 0.),$$

and the associated Bézier curve:

$$(12. - 9.47t + 9.47t^2 - 6.16t^3, -4. + 13.50t - 15.00t^2 + 5.50t^3, 3. - 6.40t + 3.81t^2 - 0.40t^3).$$

Once we have reversed the direction of the curve under the change of parameter  $t \rightarrow 1 - t$ , the control points are

$$P_0 = (5.84, 0., 0.), P_1 = (8.84, 0., 0.), P_2 = (8.84, 0.50, 0.87), P_3 = (12, -4, 3),$$

and the associated Bézier curve:

$$\alpha_B^2(t) = (5.84 + 9. t - 9. t^2 + 6.16t^3, 1.50t^2 - 5.50t^3, 2.60t^2 + 0.40t^3).$$

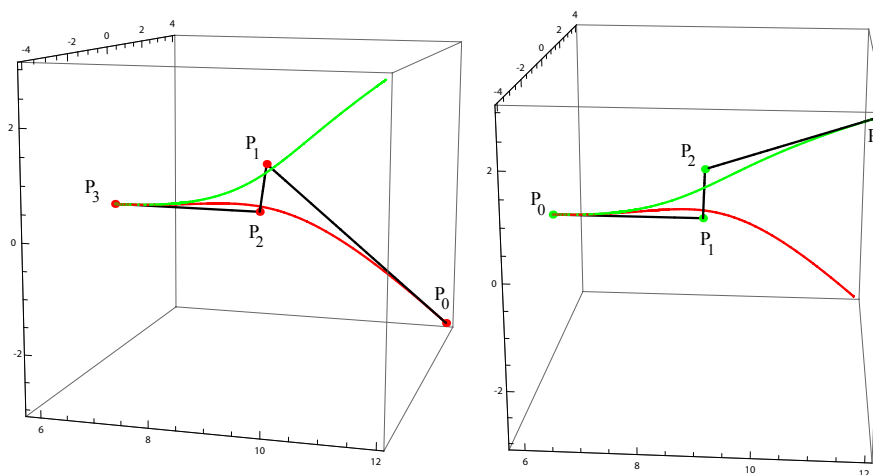


Fig. 7.- The two control polygons of the curves that model the movement of the second molecule.



In Fig. 8 we can see that curve  $\alpha_A^1$  is the one modelling the trajectory of atom 2 in the first molecule, whereas the curve  $\alpha_B^1$  describes the trajectory of atom 4 of the second molecule. The two curves do not meet but if we leave the transfer atom in the exact position of the reaction, in front of atom 4, the bond between the transfer atom and atom 4 is what we have used as the reaction vector.

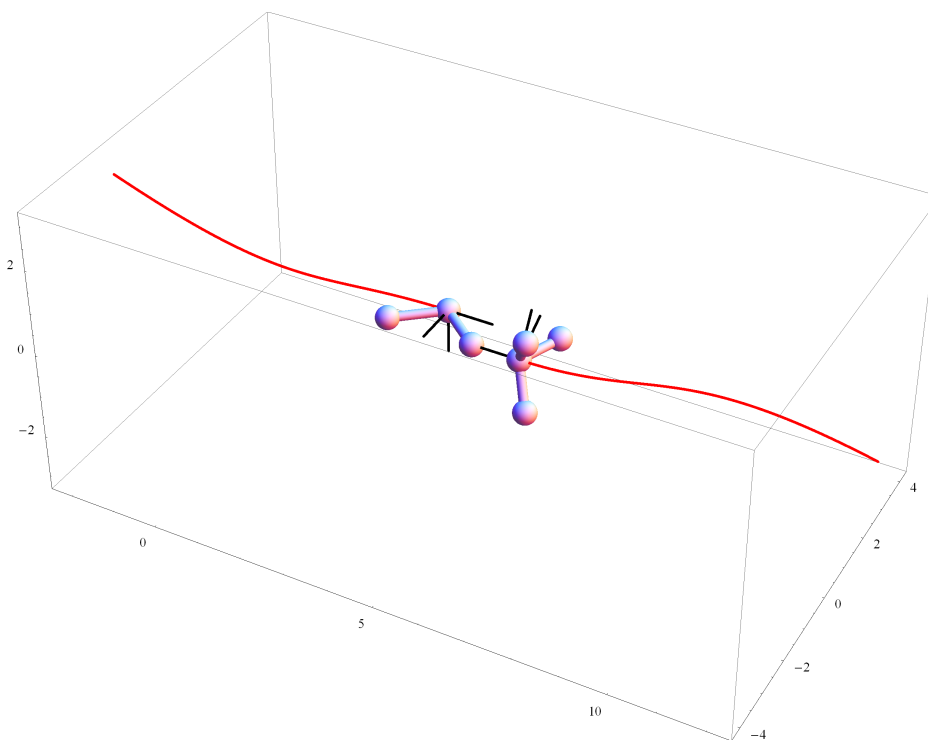


Fig. 8.- Visualization of the frames of the two molecules at the reaction point, used to define the respective Bézier curves.

## 5 Conclusion

We have seen how the techniques of Bézier curves can be applied to visualize a simple chemical reaction in three dimensional space.

The motion of each molecule (reactant or product) is determined thanks to two things:

- first, a curve which describes the trajectory of an atom of the molecule and,
- second, a way of computing how the molecule rotates around itself as it approaches or leaves the reaction point.

The first step can be solved in many ways, but the simplest one, a linear curve, would produce an unrealistic visualization of the process. Instead, we have used here Bzier curves, this is, polynomial parametrized curves of the minimum possible degree according to the restrictions we have.

For the second step, notice that rotation of the molecule as it goes along the curve can be defined using a moving frame adapted to the curve. In this way, a reference frame is attached to each molecule. When a translation and/or rotation is applied to the reference frame, this same rigid movement is applied to the whole molecule. Nevertheless, to visualize a simple chemical reaction in a natural way it is crucial to introduce no more rotation than the strictly necessary. This can be achieved thanks to the concept of Rotation Minimizing Frame.

Although we have applied these techniques to a particular reaction, they can be used with a large quantity of different reactions. We hope to apply all of this to a variety of other cases in the future.

The visualizations that we have included were programmed using *Mathematica*. It is possible to export as a *.pdb* (protein data base) file the positions of all the atoms from a discretization of the visualization. In this way the results can be used in other platforms, such as *CrystalMaker* or *Java*.

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