ANNALES DE L'I. H. P., SECTION A

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Annales de l'I. H. P., section A, tome 40, nº 3 (1984), p. 329-342
<http://www.numdam.org/item?id=AIHPA_1984__40_3_329_0>

Ann. Inst. Henri Poincaré,
Vol. 40, n° 3, 1984, p. 329-342. *Physique théorique*

On rotation and vibration motions of molecules

by

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ABSTRACT. — In the second stage of the Born-Oppenheimer approximation, a moving molecule is considered as a set of points of the euclidian space which represent the kernels of the atoms constituting the molecule; in books on Molecular Spectroscopy, under the title « separation of rotation and vibration motions », one actually defines the rotational and vibrational energies, but not the vibration motion. In the present paper we propose a mathematical definition of these last ones, and we prove that they cannot be separated from the rotation motions, in that sense that performing a purely vibrational motion, a molecule can, at the end of a finite time, come to a final configuration which is deduced from the initial one by an arbitrary pure rotation.

RÉSUMÉ. — Dans la seconde étape de l'approximation de Born-Oppenheimer, une molécule en mouvement est considérée comme un ensemble de points de l'espace euclidien, représentant les noyaux des atomes constituant la molécule; dans les ouvrages de Spectroscopie Moléculaire, sous le titre « séparation des mouvements de rotation et de vibration », on définit en réalité les énergies de rotation et de vibration, mais non les mouvements de vibration. Dans le présent travail nous proposons une définition mathématique de ces derniers, et nous montrons qu'ils ne peuvent pas être séparés des mouvements de rotation en ce sens qu'en effectuant un mouvement purement vibratoire, une molécule peut, au bout d'un temps fini, parvenir à une configuration finale qui se déduit de la configuration initiale par une rotation pure arbitraire.

§ 1. INTRODUCTION

Most of the books on Molecular Spectroscopy begin with the so-called « separation of rotations and vibrations »; this is done in terms of kinetic energy: one considers a motion of the molecule, a fixed frame and a conveniently chosen moving frame, linked to the moving molecule; the kinetic energy then appears as the sum of four terms, interpreted respectively as translational, rotational, vibrational and Coriolis energy—the last term being further neglected since it is smaller than the other three (see for instance [*5*], § 11.1). But apparently there is no theory of vibrational motions.

In this paper we give a simple mathematical definition of « vibrational velocities » for a given configuration x; they constitute a linear subspace $V_{x,\mathrm{vib}}$ of the vector space V_x of all velocities; it is defined as the orthogonal subspace of the subspace of translational and rotational velocities, with respect to a scalar product which corresponds to the kinetic energy; $V_{x,\mathrm{vib}}$ is naturally isomorphic to the « internal space of x »; but it is worth noticing that the internal space is more naturally defined as a quotient of V_x than a subspace; in this way its definition does not involve the masses of the atoms constituting the molecule.

This being done, we propose a definition of vibrational motions : a motion $x(t)$, where t is the time, is called *vibrational* if its velocity $x(t)$ belongs to $V_{x(t),\mathrm{vib}}$ for each t; physically this means that the angular momentum with respect to the center of mass is identically zero. Now a natural question arises : can one separate in some reasonable sense the translational and rotational motions (the definition of which is clear) from the vibrational ones? Our answer to this question is « no », by virtue of a (theorem 1 below) asserting that, if our molecule contains at least four atoms, one can start from some initial configuration, then perform a continuous vibrational motion, and get at the end a final configuration which is deduced from the initial one by an arbitrary pure rotation. At this point two remarks can be done : first, such motions seem to be familiar to cats who, as is well known, always fall on their legs when launched in the air; second, in the case of diatomic or triatomic molecules, the situation is very different : during a vibrational motion, a diatomic molecule will remain on some fixed straight line, and a triatomic one—in some fixed plane.

Our proofs will use various notions and results in Differential Geometry; the nonacquainted reader is referred to references [*1*] to [*4*] of our bibliography; [*3*] is a very elementary introduction to the general theory of manifolds, tangent spaces, vector fields, etc; [*4*] does the same with more physical intuition; [*1*] and [*2*] contain all useful material on principal bundles, connections, holonomy groups, etc.

We must mention that our study is purely kinematical, since we do not

introduce potential and Lagrange or Hamilton equations; we hope to return to more dynamical matters in a forthcoming paper. The author thanks J. P. Bourguignon for valuable informations in Differential Geometry, and M. Fétizon, H. P. Gervais and their colleagues chemists for introducing him to Molecular Spectroscopy.

§ 2. VARIOUS CONFIGURATION SPACES. SEPARATION OF TRANSLATIONS

We consider a molecule as a set x of n atoms $x_1, \ldots, x_n$, each x_k being identified with a point of an oriented euclidean affine space E od dimension d; roughly speaking, E is the usual space $\mathbb{R}^d$ with its usual orientation and scalar product, but without a choice of an origin; of course any choice of an origin in E yields a canonical identification of E with $\mathbb{R}^d$. We always assume $n \geqslant 2$ and $d \geqslant 2$; the cases of interest will be of course $d = 3$ but also $d = 2$ because it leads to much simpler computations. Each atom x_k is endowed with a mass m_k which is a strictly positive number; moreover two atoms cannot be at the same place; so we take as our *first configuration space* the set X_0 of all n-uples $x = (x_1, \ldots, x_n)$ with $x_k \in E$ and $x_k \neq x_{k'}$ if $k \neq k'$. This set is a manifold of a very special type, since it is an open subset of the affine space E^n; the tangent space to X_0 at a point x, denoted by $V_{0,x}$ (the traditional notation would be $T_x(X_0)$), can be identified with $(\mathbb{R}^d)^n$: it is the set of all n-uples $v = (v_1, \ldots, v_n)$ with $v_k \in \mathbb{R}^d$; physically it represents the set of all possible velocities.

We denote by $(\mid)$ the usual scalar product in $\mathbb{R}^d$ and by $\| \ \|$ the corresponding norm; we define a scalar product $B_{0,x}$ on the vector space $V_{0,x}$ by

$$B_{0,x}(v, v') = \sum_k m_k \cdot (v_k \mid v'_k);$$

it represents the kinetic energy in the sense that, if we have a motion $x(t) = (x_1(t), \ldots, x_n(t))$, the kinetic energy at the time t is

$$T = \frac{1}{2} B_{0,x(t)}(\dot{x}(t), \dot{x}(t)).$$

The family of all scalar products $B_{0,x}$ is called a riemannian structure on X_0. We shall now express in mathematical terms the well known fact that translations can be separated from other motions. We first define a vector subspace of $V_{0,x}$:

$$V_{0,x,\text{trans}} = \{ v \in V_{0,x} \mid v_1 = \ldots = v_n \};$$

its orthogonal for the scalar product $B_{0,x}$ is given by

$$V_{0,x,\text{trans}}^{\perp} = \left\{ v \in V_{0,x} \,\middle|\, \sum_k m_k v_k = 0 \right\};$$

We have

$$\begin{aligned}\dim V_{0,x,\text{trans}}^{\perp} &= \dim V_{0,x} - \dim V_{0,x,\text{trans}} \\ &= nd - d = (n-1)d\,.\end{aligned}$$

The family of all subspaces $V_{0,x,\text{trans}}^{\perp}$ is a particular case of the notion of *distribution of tangent subspaces*; we recall that such a distribution (W_x) is said to be *completely integrable* if for each point x there exists a submanifold containing x and having $W_{x'}$ as its tangent space at each point x'. In the present case the distribution *is completely integrable*, the submanifold containing x being the set of all x' such that $\Omega_{x'} = \Omega_x$ (here Ω_x denotes as usual the center of mass of the configuration x). From now on we shall restrict ourselves to such a submanifold and we shall identify E with $\mathbb{R}^d$ taking Ω_x as origin.

So our second configuration space is

$$X_1 = \left\{ x \in X_0 \,\middle|\, \sum_k m_k x_k = 0 \right\}.$$

In this space X_1 we let act the group $G = SO(d)$ of rotations in $\mathbb{R}^d$:

$$g \cdot x = (g \cdot x_1, \ldots, g \cdot x_n) \qquad \forall g \in G,\ x \in X_1\,;$$

with each x we associate its orbit $G \cdot x = \{ g \cdot x \}$ and its stabilizer (or isotropy subgroup):

$$G_x = \{ g \in G \mid g \cdot x = x \}\,;$$

G_x can be described as follows. Denote by F_x the vector subspace of $\mathbb{R}^d$ generated by $x_1, \ldots, x_n$ and by $F_x^{\perp}$ its orthogonal; then an element of G_x is equal to the identity in F_x and to an arbitrary rotation in $F_x^{\perp}$; in particular G_x is reduced to the identity if and only if $\dim F_x = d$ or $d - 1$; this condition will be useful in what follows. So we define our third and final configuration space X as follows.

DEFINITION 1. — We denote by X the set of all n-uples $x = (x_1, \ldots, x_n)$ with $x_k \in \mathbb{R}^d$, satisfying the following conditions :

i) $x_k \neq x_{k'}$ if $k \neq k'$

ii) $\sum_k m_k x_k = 0$

iii) the dimension of the vector subspace F_x of $\mathbb{R}^d$ generated by $x_1, \ldots, x_n$ is equal to d or $d - 1$; notice that this implies $n \geqslant d$.

In the usual case $d = 3$, condition (*iii*) means that the configuration x is not linear. In the general case, X is a manifold of dimension $(n-1)d$ which is still an open subset of an affine space; one can prove, and we shall admit, that X *is always arcwise connected.*

We shall denote by V_x the tangent space to X at a point x:

$$V_x = \left\{ v = (v_1, \ldots, v_n) \mid v_k \in \mathbb{R}^d, \sum_k m_k v_k = 0 \right\}$$

and by B_x the scalar product on V_x :

$$B_x(v, v') = \sum_k m_k \cdot (v_k \mid v'_k) .$$

§ 3. THE ACTION OF ROTATIONS AND THE SUBSPACES $V_{x,\mathrm{rot}}$ AND $V_{x,\mathrm{vib}}$

Some notations.

We denote by $\Lambda^2\mathbb{R}^d$ the second exterior power of $\mathbb{R}^d$, i. e. the set of all antisymmetric tensors of order 2 on $\mathbb{R}^d$; for $x, y \in \mathbb{R}^d$ we set

$$x \wedge y = x \otimes y - y \otimes x \in \Lambda^2\mathbb{R}^d .$$

There is a unique scalar product $(\mid)$ on $\Lambda^2\mathbb{R}^d$ such that if $(e_1, \ldots, e_d)$ if an orthonormal basis in $\mathbb{R}^d$, the elements $e_i \wedge e_j$ with $i < j$ constitute an orthonormal basis in $\Lambda^2\mathbb{R}^d$. In the case $d = 3$, $x \wedge y$ is identified with a vector in the usual way (vector product).

We denote by $\underline{g} = \underline{so}(d)$ the Lie algebra of the group $G = SO(d)$; this is the set of all antisymmetric $d \times d$ real matrices; there is a unique isomorphism $\xi \mapsto R_\xi$ of $\Lambda^2\mathbb{R}^d$ onto $\underline{g}$ such that

$$R_{u \wedge v}(x) = (x \mid u) \cdot v - (x \mid v) \cdot u \qquad \forall u, v, x \in \mathbb{R}^d ;$$

if $(e_1, \ldots, e_d)$ is an orthonormal basis of $\mathbb{R}^d$ and if

$$\xi = \sum_{i<j} \xi_{ij} e_i \wedge e_j \in \Lambda^2\mathbb{R}^d ,$$

then R_ξ is the matrix with entries ξ_{ij}. In the case $d = 3$, $R_\xi(x)$ is nothing but $\xi \wedge x$, $\Lambda^2\mathbb{R}^3$ being identified with $\mathbb{R}^3$ as mentioned above. We note for later use the following formulae:

$$(3.1) \qquad (R_\xi(x) \mid y) = (\xi \mid x \wedge y) \qquad \forall x, y \in \mathbb{R}^d, \xi \in \Lambda^2\mathbb{R}^d$$

$$(3.2) \qquad (y \wedge R_\xi(x) \mid \eta) = (R_\xi(x) \mid R_\eta(y)) \qquad \forall x, y \in \mathbb{R}^d ; \xi, \eta \in \Lambda^2\mathbb{R}^d .$$

Action of rotations. Internal spaces.

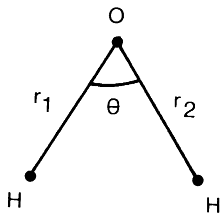
We let the group G act on X as § 2 and we recall that this action is without fixed point :

$$g \in G,\ x \in X,\ g \cdot x = x \Rightarrow g = e .$$

As a consequence of this property, the orbit X/G can be considered as a manifold which will be denoted by $\tilde{X}$; its dimension is

$$\dim \tilde{X} = \dim X - \dim G = (n-1)d - d(d-1)/2$$
$$= d(n - (d+1)/2);$$

it is now an abstract manifold, not naturally embedded in an affine space. Physically $\tilde{X}$ represents the set of all molecule forms independently of their position in $\mathbb{R}^d$; if x is a point of X and $\tilde{x}$ its image in $\tilde{X}$, we denote by $\tilde{V}_x$ (the traditional notation would be $T_{\tilde{x}}(\tilde{X})$) the tangent space to $\tilde{X}$ at $\tilde{x}$; it is called the *internal space of the configuration x.* One calls *internal coordinates* any system of local coordinates on $\tilde{X}$ in the neighbourhood of $\tilde{x}$, and also any system of coordinates on $\tilde{V}_x$. As an example we take the molecule H_2O ($d = 2$, $n = 3$); the usual internal coordinates are r_1, r_2, θ on $\tilde{X}$ and dr_1, dr_2, $d\theta$ on $\tilde{V}_x$.



Other definition of $\tilde{V}_x$.

The orbit $G \cdot x$ of any x is a submanifold of X, isomorphic with G; its tangent space is

$$V_{x,\mathrm{rot}} = \{ R_\xi(x) \mid \xi \in \Lambda^2\mathbb{R}^d \}$$

On the other hand the differential at x of the projection $X \to \tilde{X}$ is a linear mapping $V_x \to \tilde{V}_x$ which is surjective with kernel $V_{x,\mathrm{rot}}$; so $\tilde{V}_x$ can be identified with the quotient space $V_x/V_{x,\mathrm{rot}}$.

Definition of $V_{x,\mathrm{vib}}$.

We define it as the orthogonal of $V_{x,\mathrm{rot}}$ in V_x for the scalar product B_x; using formula (3.1) one immediately gets

$$V_{x,\mathrm{vib}} = \left\{ v \in (\mathbb{R}^d)^n \,\middle|\, \sum_k m_k v_k = \sum_k m_k \cdot x_k \wedge v_k = 0 \right\}.$$

Clearly $V_{x,\text{vib}}$ *depends on the masses* $m_1, \ldots, m_n$; but it is canonically isomorphic with $\tilde{V}_x$ which *does not depend on the masses* : in fact $V_{x,\text{vib}}$ being a supplementary of $V_{x,\text{rot}}$ in V_x, the restriction to $V_{x,\text{vib}}$ of the projection $V_x \to \tilde{V}_x$ is an isomorphism.

Definition of vibrational curves.

We first define a *smooth curve* on a manifold X as a mapping γ from some interval $[a, b]$ to X which is continuously differentiable; its derivative at a point t is an element $\dot{\gamma}(t)$ of $V_{\gamma(t)}$. We then define a *curve* as a mapping γ which is continuous and piecewise continuously differentiable; thus it has for each t a left derivative $\dot{\gamma}_1(t)$ and a right derivative $\dot{\gamma}_r(t)$, which are distinct only for a finite number of t's.

DEFINITION 2. — We say that a curve γ on X is *vibrational* if $\dot{\gamma}_1(t)$ and $\dot{\gamma}_r(t)$ belong to $V_{\gamma(t),\text{vib}}$ for every t; physically this means that the angular momentum with respect to 0 is identically zero.

The main aim of this paper is the following result:

THEOREM 1. — *We assume that $n > d$. Then every two points of an arbitrary* G-*orbit in* X *can be joined by a smooth vibrational curve ; every two points of* X *can be joined by a vibrational curve.*

Its proof in the general cas will be given in § 4; a more elementary proof in a particular case ($d = 2$, $n = 3$) will be given in § 5; this case is simpler because SO(2) is abelian.

In the case where $n = d$ the situation is quite different, as the following result shows:

PROPOSITION 1. — *If $n = d$ and if $x(t)$ is a smooth vibrational curve, then the hyperplane $F_{x(t)}$ is constant.*

Proof. — We first remark that $\dim F_x = d - 1$ for every $x \in X$.

a) We claim that for each $v \in V_{x,\text{vib}}$ we have $v_k \in F_x$ $\forall k$. To prove this we can assume $(x_1, \ldots, x_{d-1})$ is a basis of F_x; we take a basis (e_i) of $\mathbb{R}^d$ such that

$$e_i = x_i \quad \text{if} \quad i = 1, \ldots, d-1$$
$$e_d \in F_x^{\perp};$$

we decompose v_k on this basis, with coordinates $v_{k,i}$; condition $\Sigma m_k v_k = 0$ implies

$$\sum_k m_k v_{k,d} = 0; \tag{3.3}$$

on the other hand, since

$$m_d x_d = - m_1 x_1 - \ldots - m_{d-1} x_{d-1},$$

condition $\Sigma m_k \cdot x_k \wedge v_k = 0$ implies

$$(3.4) \qquad v_{k,d} - v_{d,d} = 0 \qquad \forall k = 1, \ldots, d-1;$$

(3.3) and (3.4) together imply $v_{k,d} = 0 \ \forall k$, whence $v_k \in F_x$.

b) To prove our proposition we choose a unitary vector $y(t)$ orthogonal to $F_{x(t)}$ and depending continuously on t; $(y(t) \mid x_k(t)) = 0$ implies

$$(\dot{y}(t) \mid x_k(t)) + (y(t) \mid \dot{x}_k(t)) = 0;$$

the second member is zero by part *a*); $\dot{y}(t)$ is orthogonal to $y(t)$, hence belongs to $F_{x(t)}$; being orthogonal to all $x_k(t)$'s which generate $F_{x(t)}$, $\dot{y}(t)$ is null. Q. E. D.

§ 4. PROOF OF THEOREM 1 IN THE GENERAL CASE

Let us first formulate a natural question: is the distribution of tangent subspaces $V_{x,\mathrm{vib}}$ completely integrable in the sense defined in § 2? The answer is provided by Frobenius theorem: a distribution of tangent subspaces W_x is completely integrable if and only if for every pair of vector fields $v(x)$ and $v'(x)$ satisfying $v(x), v'(x) \in W_x$ for every x, their Lie bracket $[v, v']$ satisfies the same condition. Lemmas 2 and 3 below will show that in our case the answer is « no » and in some sense « definitely no ».

We begin with a lemma giving the explicit form of the orthogonal projection $P_x : V_x \to V_{x,\mathrm{rot}}$ (« orthogonal » is always with respect to the scalar product B_x). We first recall the definition of the inertia operator A_x of the configuration x : A_x is the linear operator in $\Lambda^2 \mathbb{R}^d$ defined by

$$A_x(\xi) = \sum_k m_k (x_k \wedge R_\xi(x_k));$$

in the case $d = 3$, $A_x(\xi)$ is the angular momentum with respect to 0 of the velocity corresponding to the infinitesimal rotation R_ξ. Using formula (3.2) one gets

$$(A_x(\xi) \mid \eta) = \sum_k m_k (R_\xi(x_k) \mid R_\eta(x_k))$$

which shows that A_x is symmetric and positive definite; therefore it has an inverse A_x^{-1}.

LEMMA 1. — *For every* $v \in V_x$, $P_x(v)$ *is given by*

$$(P_x(v))_k = R\left(A_x^{-1}\left(\sum_{k'} m_{k'} \cdot x_{k'} \wedge v_{k'}\right)\right)(x_k)$$

(*we write here* $R(\xi)$ *instead of* R_ξ *for notational convenience*).

Proof. — Calling v'_k the righthand side, we must prove that $v' - v$ belongs to $V_{x,\text{vib}}$, that is

$$\sum_k m_k \cdot x_k \wedge (v'_k - v_k) = 0 .$$

But

$$\begin{aligned}\sum_k m_k \cdot x_k \wedge (v'_k - v_k) \\ &= \sum_k m_k \cdot x_k \wedge R\left(A_x^{-1}\left(\sum_{k'} m_{k'} \cdot x_{k'} \wedge v_{k'}\right)\right)(x_k) - \sum_k m_k \cdot x_k \wedge v_k \\ &= A_x\left(A_x^{-1}\left(\sum_{k'} m_{k'} \cdot x_{k'} \wedge v_{k'}\right)\right) - \sum_k m_k \cdot x_k \wedge v_k = 0 .\end{aligned}$$

LEMMA 2. — *Let us consider two vector fields* $v(x)$, $v'(x)$ *satisfying* $v(x)$, $v'(x) \in V_{x,\text{vib}}$ *for every* x. *Then*

$$\sum_k m_k \cdot x_k \wedge [v, v']_k(x) = -2 \sum_k m_k \cdot v_k(x) \wedge v'_k(x) .$$

Proof. — We recall the formula giving, for an arbitrary manifold X, the Lie bracket of two vector fields v, v' in local coordinates $(x_1, \ldots, x_m)$: if

$$v = \sum_i a_i \cdot \partial/\partial x_i, \qquad v' = \sum_i a'_i \cdot \partial/\partial x_i ,$$

then

$$[v, v'] = \sum_i \sum_j (a_j \cdot \partial a'_i/\partial x_j - a'_j \cdot \partial a_i/\partial x_j) \cdot \partial/\partial x_i ,$$

In our case one can take as coordinates of a point $x \in X$ the numbers $x_{k,i}$, cartesian coordinates of x_k in a given basis of $\mathbb{R}^d$; the proof is now an easy but tedious computation.

LEMMA 3. — *Let* $x \in X$ *be such that* $x_1, \ldots, x_n$ *generate* $\mathbb{R}^d$. *Then the elements* $\Sigma m_k \cdot v_k \wedge v'_k$ *generate* $\Lambda^2 \mathbb{R}^d$ *when* v *and* v' *run over* $V_{x,\text{vib}}$.

Proof. — Since the set $(x_1, \ldots, x_n)$ generates $\mathbb{R}^d$, it contains a basis and

we can suppose $(x_1, \ldots, x_d)$ is a basis; then the set of elements $x_k \wedge x_{k'}$ with $1 \leqslant k < k' \leqslant d$ is a basis of $\Lambda^2\mathbb{R}^d$. Clearly it is enough to prove that $x_1 \wedge x_2$ is of the form $\Sigma m_k \cdot v_k \wedge v'_k$ with $v, v' \in \mathrm{V}_{x,\mathrm{vib}}$.
To do this we decompose x_{d+1} on the basis $(x_1, \ldots, x_d)$:

$$x_{d+1} = \sum_{k=1}^{d} r_k x_k$$

and we set

$$r = \begin{cases} \displaystyle\sum_{k=3}^{d} r_k - 1 & \text{if} \quad d \geqslant 3 \\ -1 & \text{if} \quad d = 2; \end{cases}$$

we take three arbitrary real numbers a_1, a_2, a_3 and we define $v_1, \ldots, v_n$ as follows :

$$m_1v_1 = \left(\frac{1}{2}(-a_3 + r_2a_1 - r_1a_2) + ra_1\right) \cdot x_1 + \frac{1}{2}(a_3 + r_2a_1 - r_1a_2) \cdot x_2$$

$$m_2v_2 = \frac{1}{2}(a_3 - r_2a_1 + r_1a_2) \cdot x_1 + \left(\frac{1}{2}(-a_3 - r_2a_1 + r_1a_2) + ra_2\right) \cdot x_2$$

$$m_kv_k = -r_k(a_1x_1 + a_2x_2) \quad \text{for} \quad k = 3, \ldots, d$$

$$m_{d+1}v_{d+1} = a_1x_1 + a_2x_2$$

$$m_kv_k = 0 \qquad \text{for} \quad k > d+1\,.$$

It is easy to check that v belongs to $\mathrm{V}_{x,\mathrm{vib}}$. We define similarly v' by means of numbers a'_i. We have

$$\sum_k m_k \cdot v_k \wedge v'_k = \sum_{1 \leqslant i < j \leqslant 3} c_{ij}(a_ia'_j - a_ja'_i) \cdot x_1 \wedge x_2$$

where

$$c_{12} = -r(r_1/m_1 + r_2/m_2)/2 + \sum_{k=1}^{d} r_k^2/m_k + 1/m_{d+1}$$

$$c_{13} = r/2m_1 + (m_1 + m_2)r_2/2m_1m_2$$

$$c_{23} = -r/2m_2 - (m_1 + m_2)r_1/2m_1m_2\,.$$

We have to prove that c_{12}, c_{13}, c_{23} cannot be simultaneously equal to 0; but if $c_{13} = c_{23} = 0$ we have

$$c_{12} = r^2/(m_1 + m_2) + \sum_{k=1}^{d} r_k^2/m_k + 1/m_{d+1}$$

which is clearly strictly positive.

LEMMA 4. — *Let $x \in \mathrm{X}$ and $g \in \mathrm{G} = \mathrm{SO}(d)$. Then x and $g \cdot x$ can be joined by a smooth vibrational curve.*

Proof. — *a*) We denote by π the projection $\mathrm{X} \to \tilde{\mathrm{X}}$; since G acts on X without fixed points, the triple $(\mathrm{X}, \tilde{\mathrm{X}}, \pi)$ is a *principal bundle with group* G and is locally trivial, as easily seen; on this bundle we have a *connection* : the differential 1-form ω on X with values in $\underset{\sim}{g}$ such that for every x in X and v in V_x, $\omega_x(v)$ is the unique element $\mathrm{T} \in \underset{\sim}{g}$ satisfying $\mathrm{T}(x) = \mathrm{P}_x(v)$; by lemma 1 we have

$$\omega_x(v) = \mathrm{R}\left(\mathrm{A}_x^{-1}(\Sigma m_k \cdot x_k \wedge v_k)\right). \tag{4.1}$$

Our connection ω has a *curvature* Ω: the differential 2-form on X with values in $\underset{\sim}{g}$ characterized by the conditions:

$$\Omega_x(v, v') = 0 \qquad \text{if} \quad v \text{ or } v' \text{ belongs to } \mathrm{V}_{x,\mathrm{rot}}$$

and

$$\Omega_x(v, v') = -\frac{1}{2}\omega_x([v, v']) \tag{4.2}$$

if v and v' belong to $\mathrm{V}_{x,\mathrm{vib}}$ and are extended to vector fields satisfying $v(x), v'(x) \in \mathrm{V}_{x,\mathrm{vib}}$ for every x. By formula (4.1) and lemme 2, formula (4.2) becomes

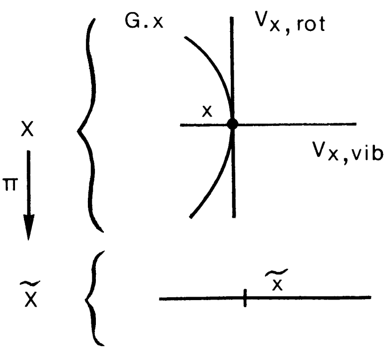
$$\Omega_x(v, v') = \mathrm{R}\left(\mathrm{A}_x^{-1}(\Sigma m_k \cdot v_k \wedge v'_k)\right). \tag{4.3}$$

b) Let us now consider a smooth curve η on $\tilde{\mathrm{X}}$ with parameter t in some interval $[a, b]$; set $\tilde{x}_0 = \eta(a)$ and choose x_0 in $\pi^{-1}(\tilde{x}_0)$; it is known that there exists a unique smooth vibrational curve γ on X above η and starting from x_0, i. e. satisfying

$$\pi(\gamma(t)) = \eta(t) \qquad \forall t$$
$$\gamma(a) = x_0;$$

this γ will be called the *vibrational lift* of η starting from x_0.

N. B. Differential geometers would say « horizontal lift » instead of « vibrational lift »; they call $\mathrm{V}_{x,\mathrm{rot}}$ and $\mathrm{V}_{x,\mathrm{vib}}$ respectively « vertical » and « horizontal subspaces » of V_x, because of the opposite picture.



c) Now suppose η is a loop, i. e. $\eta(b) = \eta(a) = \tilde{x}_0$; then

$$\gamma(b) \in \pi^{-1}(x_0) = G \cdot x_0 ;$$

let us denote $\gamma(b)$ by $f(\eta, x_0)$; we want to prove that when x_0 is fixed but the loop η varies, the point $f(\eta, x_0)$ runs over all of $G \cdot x_0$.

d) There exists a unique element $g(\eta, x_0)$ in G such that

$$f(\eta, x_0) = g(\eta, x_0) \cdot x_0 ;$$

one can show that, when x_0 is fixed but η varies, the elements $g(\eta, x_0)$ form a Lie subgroup of G; this subgroup is called the *holonomy group* at x_0 and will be denoted by $H(x_0)$; its Lie algebra is a Lie subalgebra $\underline{h}(x_0)$ of $\underline{g}$. Now the *holonomy theorem* (actually its easiest part) asserts that $\underline{h}(x_0)$ contains all elements of $\underline{g}$ of the form $\Omega_{x_0}(v, v')$ with $v, v' \in V_{x_0,\mathrm{vib}}$; on the other hand, if x_0 is such that $x_{01}, \ldots, x_{0n}$ generate $\mathbb{R}^d$, formula (4.3) and lemma 3 show that $\underline{h}(x_0) = \underline{g}$, whence $H(x_0) = G$; but since X is connected, all holonomy groups are conjugated, hence $H(x_0) = G$ for all $x_0 \in X$. This proves our assertion.

N. B. In general books on Differential Geometry define the holonomy group by taking curves η on X which are piecewise continuously differentiable instead of smooth; but one can prove that both definitions are equivalent.

Proof of theorem 1. — The first assertion is precisely lemma $\tilde{4}$. To prove the second one, take x and y in X, and a smooth curve η on $\tilde{X}$ joining $\tilde{x}$ to $\tilde{y}$; its vibrational lift γ_1 joins x to some point y' of $G \cdot y$; by lemma 4 there is a smooth vibrational curve γ_2 joining y' to y; it is now sufficient to take the union of γ_1 and γ_2; notice that at the point y', the left and right derivatives are not necessarily identical.

§ 5. OTHER PROOF OF THEOREM 1 IN THE CASE WHERE $d = 2$, $n = 3$

We fix an orthonormal basis (e_1, e_2) in $\mathbb{R}^2$.

a) Here the manifold X as defined in definition 1 is the set of all triples $x = (x_1, x_2, x_3)$ with $x_k \in \mathbb{R}^2$ such that $x_k \neq x_{k'}$ if $k \neq k'$ and $\Sigma m_k x_k = 0$. But what actually interest us is to give a more elementary proof of lemma 4 in the case where x_1, x_2, x_3 generate $\mathbb{R}^2$; then (x_1, x_2) is a basis. Thus we can redefine X as the set of all bases (x_1, x_2) in $\mathbb{R}^2$, and x_3 is defined by $x_3 = -(m_1 x_1 + m_2 x_2)/m_3$; here $G = SO(2)$; $\tilde{X}$ can be described as the set of all pairs $y = (y_1, y_2)$ where

$$y_1 = q_1 e_1, \qquad q_1 > 0$$
$$y_2 = q_2 e_1 + q_3 e_2, \quad q_3 \neq 0;$$

thus the coordinates on $\tilde{X}$ are q_1, q_2, q_3 with $q_1 > 0$, $q_3 \neq 0$.

b) Let us now consider a smooth curve η on $\tilde{X}$:

$$\eta(t) = (q_1(t), q_2(t), q_3(t)), \qquad t \in [a, b]$$

and look for the vibrational lift γ on η; $\gamma(t)$ is of the form

$$\gamma(t) = (x_1(t), x_2(t))$$

where

$$x_k(t) = \begin{pmatrix} \cos\theta(t) & -\sin\theta(t) \\ \sin\theta(t) & \cos\theta(t) \end{pmatrix} \cdot y_k(t)$$

and θ is an unknown function of t. The curve γ is vibrational if and only if

$$\sum_{k=1}^{3} m_k \cdot x_k(t) \wedge \dot{x}_k(t) = 0 \quad \forall t;$$

an easy computation shows that this relation is equivalent to the elementary differential equation

$$\dot{\theta} = a_1(q)\cdot\dot{q}_1 + a_2(q)\cdot\dot{q}_2 + a_3(q)\cdot\dot{q}_3 \tag{5.1}$$

where

$$a_1(q) = m_1 m_2 q_3/\mathrm{D}(q)$$
$$a_2(q) = m_2(m_2 + m_3)q_3/\mathrm{D}(q)$$
$$a_3(q) = -\, m_2(m_1 q_1 + (m_2 + m_3)q_2)/\mathrm{D}(q)$$
$$\mathrm{D}(q) = m_1(m_1 + m_3)q_1^2 + m_2(m_2 + m_3)(q_2^2 + q_3^2) + 2m_1 m_2 q_1 q_2;$$

we notice that $\mathrm{D}(q)$ is strictly positive.
Relation (5.1) implies

$$\theta(b) - \theta(a) = \int_a^b (a_1\dot{q}_1 + a_2\dot{q}_2 + a_3\dot{q}_3)\cdot dt = \int_\eta \omega$$

where ω is the following differential 1-form on X:

$$\omega = a_1 \cdot dq_1 + a_2 \cdot dq_2 + a_3 \cdot dq_3;$$

this ω is more or less equivalent to the 1-form ω introduced in the proof of lemma 4.

c) Let us now suppose η is a loop, i. e. $\eta(a) = \eta(b)$; Stokes theorem says that

$$\theta(b) - \theta(a) = \int_\Sigma d\omega \tag{5.2}$$

where Σ is an arbitrary surface in $\tilde{X}$ bounded by η and conveniently oriented, and

$$d\omega = \sum_{i<j} (\partial a_j/\partial q_i - \partial a_i/\partial q_j)\cdot dq_i \wedge dq_j.$$

An easy computation shows that

$$\partial a_2/\partial q_1 - \partial a_1/\partial q_2 = -2m_1m_2m_3(m_1+m_2+m_3)\cdot q_1q_3/\mathrm{D}(q)^2 .$$

If we take a curve η such that q_3 is a constant k, (5.2) becomes

$$\theta(b) - \theta(a) = -2m_1m_2m_3(m_1+m_2+m_3)k\int_\Sigma q_1\cdot \mathrm{D}^{-2}(q)\cdot dq_1 \wedge dq_2 ;$$

clearly the righthand side can take arbitrary values, which proves lemma 4 in our particular case.

§ 6. REMARKS ON SIMILAR SITUATIONS

Given a differential 1-form ω on a manifold X, one can call *horizontal* (by analogy with § 4 above) any curve on X annihilating ω; we shall illustrate this notion by two familiar examples.

Firstly, in Thermodynamics, taking for ω what is usually denoted by δQ, a horizontal curve will be what is called *adiabatic process*; but in that case, ω admits an integrating factor since $\omega = \mathrm{T}\cdot d\mathrm{S}$ where T is the temperature and S—the entropy; moreover in every neighbourhood of any point M there are points which are not accessible from M by an adiabatic process. In our case the conclusions are the opposite ones.

Secondly, let us take for X the set of all triples (x, y, θ) where x and y are real numbers and θ is an angle; we identify such a triple with the point $\mathrm{M} = (x, y)$ and the straight line D through M with angle θ; let us further take the 1-form $\omega = \cos\theta\cdot dy - \sin\theta\cdot dx$. Then a curve $(\mathrm{M}(t), \mathrm{D}(t))$ is horizontal if and only if $\mathrm{D}(t)$ is tangent to the curve $\mathrm{M}(t)$; in that case the conclusion is the same as in our case, since every two pairs $(\mathrm{M}_1, \mathrm{D}_1)$, $(\mathrm{M}_2, \mathrm{D}_2)$ can be joined by a horizontal curve.

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(Manuscrit reçu le 5 Mai 1983)