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

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Annales de l'I. H. P., section A, tome 47, nº 2 (1987), p. 199-219
<http://www.numdam.org/item?id=AIHPA_1987__47_2_199_0>

Ann. Inst. Henri Poincaré,
Vol. 47, nº 2, 1987, p. 199-219. *Physique théorique*

A geometric setting for classical molecular dynamics

by

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ABSTRACT. — In studying the « internal » motions of a molecule (a many-particle system), use has been made of the Eckart frame, relative to which the molecule moves without rotation. This paper shows, on the geometry of the center-of-mass system due to A. Guichardet, that the Eckart frame exists for any configuration of the non-rigid molecule, but not uniquely. The main purpose of this article is then to apply the reduction method of Marsden-Weinstein to the Hamiltonian system which describes the classical molecular dynamics and is defined on the cotangent bundle of the center-of-mass system, in order to eliminate the rotation motion. If the angular momentum is not zero, nor the molecule is restricted on a fixed plane, the reduced phase space is larger than the cotangent bundle of the internal space and carries the two-form to which the source of the Coriolis force is attributed.

RÉSUMÉ. — Dans l'étude des mouvements « internes » d'une molécule (un système de plusieurs corps), on emploie un repère d'Eckart, par rapport auquel la molécule effectue un mouvement sans rotations. On montre, à la suite d'un travail d'A. Guichardet, qu'il existe un repère d'Eckart pour une configuration arbitraire de la molécule, mais pas de façon unique. Le but principal de ce travail est alors d'appliquer la méthode de réduction de Marsden-Weinstein au système hamiltonien qui décrit la dynamique classique de la molécule et est défini sur le fibré cotangent au système du centre-de-gravité, pour éliminer les mouvements de rotation. Si le moment cinétique n'est pas nul, ou si la molécule n'est pas limitée à un plan fixe, l'espace de phases réduit est plus grand que le fibré cotangent à l'espace interne, et muni d'une 2-forme à laquelle est attribuée la source de la force de Coriolis.

1. INTRODUCTION

In this paper, a molecule means a system of particles or atomic nuclei, which is the picture of molecules in the Born-Oppenheimer approximation. The theory of small vibrations of molecules is found in any book on molecular dynamics. However, if one wishes to study much more of molecular motions than the small vibrations, one gets involved with difficulty caused by the non-rigidity of molecules. The problem of separating the vibration motions from the collective motions has been receiving continuous attention both in classical and quantum mechanics. Here the collective motions denote the translation and rotation motions. In any respect, the problem of the separation makes one study what is meant by the Eckart condition of the translationless and rotationless constraints. In other words, one has to investigate what the internal motion of the molecule is. For the Eckart condition, see Eckart [*1*], Louck and Galbraith [*2*], and Sutcliffe [*3*].

A. Guichardet [*4*] defined rigorously the vibration motions, and thereby showed that the vibration motions can not be separated from the rotation motions on the theory of connections in differential geometry. According to him, performing a purely vibrational motion, a molecule in $\mathbf{R}^d$ 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. The point of his theory is the observation that a center-of-mass system is made into a principal fiber bundle with rotation group $SO(d)$ as the structure group, on which a connection is defined by the Eckart condition of rotationless constraint. The internal space for the molecules is then the base manifold of that principal fiber bundle.

On the basis of the connection theory for the center-of-mass system, this paper shows that the Eckart frame exists for any configuration of the molecule, but not uniquely, where the Eckart frame is a moving frame relative to which the molecule moves without rotation. For this reason, the Eckart frame is not suitable for dynamics of non-rigid molecules. The purpose of this paper is then to discuss how the collective motions of the non-rigid molecules are gotten rid of in the Hamiltonian formalism, without reference to the Eckart frame.

Hamiltonian mechanics of non-rigid molecules is set up on the cotangent bundle of the center-of-mass system. Elimination of the angular momentum will be carried out by using the reduction theorem of Marsden and Weinstein [*5*]. The reduced Hamiltonian system will be interpreted as a dynamical system free of collective motions.

This paper is organized as follows. In Section 2, a brief review is given of Guichardet's work on which this article is based. The center-of-mass system for a molecule is described as a principal fiber bundle with rotation group as the structure group. The internal space of the molecule is then defined as the base manifold of the principal fiber bundle, which is, so to speak, the set of all molecule forms independent of their position in a laboratory frame.

According to Guichardet [*4*], a connection is naturally defined on that principal fiber bundle. Indeed, the Eckart condition of rotationless constraint defines a « vibrational » subspace of the tangent space at every point of the total bundle space. The fact that this connection has non-vanishing curvature makes it impossible to separate vibration from rotation. Even infinitesimal vibrations are coupled to give necessarily rise to infinitesimal rotations. Hence the Eckart condition in the original form is not effective for deformable molecules. Sternberg [*6*] and Kobayashi and Nomizu [*7*] contains all useful materials on principal fiber bundles, connections, etc. For physical intuition to the fiber bundle theory, Bleecker [*8*], Nash and Sen [*9*], and Eguchi, Gilkey, and Hanson [*10*] are helpful.

Section 3 contains a study of the Eckart frame [*2*] in terms of the connection theory. It is shown that one can find a moving frame, called the Eckart frame, relative to which the molecule moves without rotation. However, the frame depends inevitably on the molecular motion chosen, so that it is not unique for any configuration of the molecule.

In Sections 4 and 5, Hamiltonian mechanics for non-rigid molecules is set up on the cotangent bundle of the configuration space. See Arnold [*11*] and Abraham and Marsden [*12*] for Hamiltonian mechanics in differential geometric setting. In Sec. 4, reduction of the molecular Hamiltonian system is performed by using the linear and angular momentums. The reduction by the linear momentum yields the cotangent bundle of the center-of-mass system. This is a well-known fact. However, the cotangent bundle of the center-of-mass system is not reduced in general to the cotangent bundle of the internal space by using the angular momentum. The reduced phase space is larger than the cotangent bundle of the internal space. This implies that the molecular motions should be described in terms of internal coordinates and their conjugate momentums plus some other variables, so that the motions are not considered as internal in general. The reduction by the angular momentum also accounts for the source of the Coriolis force. Indeed, the reduced symplectic form is written as a sum of a « canonical » two-form plus the exterior derivative of the inner product of the so(d)-valued connection form and the angular momentum value in so(d). This expression is reminiscent of a symplectic form which is used in describing motions of a charged particle in a magnetic field [*13*]. In the case of $d = 3$, one has so(3) $\cong \mathbf{R}^3$, the same space as the molecule moves in, and therefore can picture that the molecule moves in response to the magnetic-like field (i. e., acted by the Coriolis force), depending on its attitude to a fixed angular momentum vector. This also accounts for why the molecular motion is not internal, but depends on its attitude in $\mathbf{R}^d$.

Section 5 shows that the kinetic energy is broken up into vibrational and rotational energies. No Coriolis term appears. However this does not mean that no Coriolis interaction appears. It comes into dynamics through the two-form stated above. It is also shown that the vibrational energy defines a Riemannian metric on the internal space, which can be thought of as a generalization of Wilson's G matrix [*14*]. The rotational energy will define a function (or a centrifugal potential) on the reduced phase space, when the conservation of angular momentum is taken into account.

Section 6 is a summary of the reduced Hamiltonian system as a statement of theorems in this paper.

2. SETTINGS ON THE CENTER-OF-MASS SYSTEM

This section is a review of Guichardet's work [*4*]. For use in the following sections, we reproduce necessary definitions and results.

2.1. A principal fiber bundle.

We consider a molecule as a set of N particles or atomic nuclei, whose position in $\mathbf{R}^d$ we denote by $x_1, \ldots, x_N$. We always assume that $N \geqq 2$ and $d \geqq 2$. The standard inner product in $\mathbf{R}^d$ is denoted by the round brackets $(\mid)$. Each particle at x_k is endowed with a mass $m_k > 0$. Let Q_0 be the set of all ennuples $x = (x_1, \ldots, x_N)$ with $x_j \neq x_k$ for $j \neq k$, which is an open submanifold of $(\mathbf{R}^d)^N$. The tangent space to Q_0 at x, denoted by $T_x(Q_0)$, consists of all ennuples $v = (v_1, \ldots, v_N)$ with $v_j \in \mathbf{R}^d$, which is identified with $(\mathbf{R}^d)^N$. Each tangent space is endowed with a scalar product by

$$K_x(u, v) = \Sigma m_k(u_k \mid v_k) \tag{2.1}$$

for $u = (u_1, \ldots, u_N)$ and $v = (v_1, \ldots, v_N)$ of $T_x(Q_0)$.

Eliminating the translation motions of the molecule, we get the center-of-mass system;

$$Q = \{ x \in Q_0 \mid \Sigma m_k x_k = 0 \} . \tag{2.2}$$

We denote the induced metric on the center-of-mass system Q by the same letter K for notational convenience.

Elimination of rotations is to be performed to get the « internal » space. Let $SO(d)$ be the rotation group acting on $\mathbf{R}^d$. An induced action of $SO(d)$ on the center-of-mass system Q is expressed in the form

$$gx = (gx_1, \ldots, gx_N) , \tag{2.3}$$

because for x with $\Sigma m_k x_k = 0$, one has $\Sigma m_k g x_k = 0$.

We assume that the molecule is in a generic position, i. e., the position vectors x_k, $k = 1, \ldots, N$, span a hyperplane in $\mathbf{R}^d$ or the whole space $\mathbf{R}^d$. Note that this assumption implies that $N \geqq d$. Then the SO(d) acts without fixed point, so that the orbit space Q/SO(d), denoted by M, becomes a manifold. We mean by π the natural projection of Q onto M. Physically, the M is a space of all molecule forms independent of their position in $\mathbf{R}^d$, and hence we call M the internal space for the molecule. For the three-body system, it is known what space the internal space is diffeomorphic to (see [*15-16*]).

We thus have come to the conclusion that the center-of-mass system Q is a principal fiber bundle over M with structure group SO(d).

We here mention that the structure group SO(d) acts on Q to the left, contrary to the usual definition in which the action of structure group is « to the right » [*7*].

2.2. **The connection due to Guichardet.**

Following Guichardet [*4*], we now show that the Eckart condition of rotationless constraint defines a connection on the center-of-mass system Q. Since connections are described in terms of the Lie algebra of the structure group, we have to start with the Lie algebra of SO(d).

Let $\Lambda^2\mathbf{R}^d$ be the linear space of all antisymmetric tensor of order 2 on $\mathbf{R}^d$. The $\Lambda^2\mathbf{R}^d$ is endowed with a natural inner product, denoted by the same symbol as in $\mathbf{R}^d$, by

$$(u \wedge v \mid x \wedge y) = \begin{vmatrix} (u \mid x) & (u \mid y) \\ (v \mid x) & (v \mid y) \end{vmatrix} . \tag{2.4}$$

Definition (2.4) extends to all two-vectors through the linearity. If $\{ e_1, \ldots, e_d \}$ is an orthogonal basis in $\mathbf{R}^d$, $e_i \wedge e_j$ with $i < j$ constitute an orthogonal basis in $\Lambda^2\mathbf{R}^d$. For two-vectors

$$\xi = \sum_{i<j} \xi_{ij} e_i \wedge e_j , \qquad \zeta = \sum_{k<l} \zeta_{kl} e_k \wedge e_l , \tag{2.5}$$

Definition (2.4) gives

$$(\xi \mid \zeta) = \sum_{i<j} \xi_{ij} \zeta_{ij} . \tag{2.6}$$

Let so(d) be the Lie algebra of SO(d), consisting of antisymmetric $d \times d$ real matrices. The Lie algebra so(d) is identified with $\Lambda^2\mathbf{R}^d$ by an isomorphism of $\Lambda^2\mathbf{R}^d$ onto so(d): $\xi \to \mathrm{R}_\xi$ such that

$$\mathrm{R}_{u \wedge v}(x) = (v \mid x)u - (u \mid x)v \qquad \text{for} \quad u, v, x \in \mathbf{R}^d . \tag{2.7}$$

Notice that our definition of R is different from that in [4] in sign. For $\xi \in \Lambda^2\mathbf{R}^d$ given in (2.5) and $x = \Sigma x^j e_j \in \mathbf{R}^d$, one has from (2.7)

$$R_\xi(x) = \sum_i \Big(\sum_j \xi_{ij} x_j\Big) e_i . \tag{2.8}$$

That is, R_ξ is an antisymmetric matrix with entries ξ_{ij}.

The Lie algebra so(d) carries a natural scalar product; for $\alpha, \beta \in$ so(d) the scalar product of α and β is defined by

$$(\alpha \mid \beta) = \frac{1}{2} \operatorname{tr}(\alpha\beta^{T}), \tag{2.9}$$

where the superscript T indicates the transpose. Then from (2.6) and (2.9) R becomes an isometry of $\Lambda^2\mathbf{R}^d$ onto so(d);

$$(R_\xi \mid R_\zeta) = (\xi \mid \zeta) . \tag{2.10}$$

We note here that R is equivariant with respect to the action of SO(d) on both $\Lambda^2\mathbf{R}^d$ and so(d). The action of SO(d) on $\Lambda^2\mathbf{R}^d$ is of course defined through

$$u \wedge v \to gu \wedge gv \qquad \text{for} \quad u, v \in \mathbf{R}^d , \tag{2.11}$$

and that on so(d) is the adjoint action. The equivariance has then the form

$$R_{g\xi} = g R_\xi g^{-1} . \tag{2.12}$$

The proof of (2.12) can be performed by using (2.7) and the SO(d)-invariance of the inner product.

The following formulae, easy to prove, are of great use in what follows,

$$(x \mid R_\xi(y)) = (x \wedge y \mid \xi) , \tag{2.13}$$

$$(R_\xi(x) \mid R_\zeta(y)) = (R_\xi(x) \wedge y \mid \zeta) . \tag{2.14}$$

To investigate the Eckart condition of rotationless constraint, we first define the rotational subspace $W_{x,\mathrm{rot}}$ of $T_x(Q)$. Let R_ξ denote an antisymmetric matrix with entries ξ_{ij} as in (2.8). Then the infinitesimal generator of the action of $g(t) = \exp tR_\xi$ is given at $x = (x_1, \ldots, x_N)$ by

$$\frac{d}{dt} g(t)x \,|_{t=0} = R_\xi(x) = (R_\xi(x_1), \ldots, R_\xi(x_N)) . \tag{2.15}$$

The $R_\xi(x)$ is known also as a fundamental vector field [7]. Thus we have the rotational subspace of $T_x(Q)$:

$$W_{x,\mathrm{rot}} = \{ R_\xi(x) \mid \xi \in \Lambda^2\mathbf{R}^d \} . \tag{2.16}$$

The orthogonal complement $W_{x,\mathrm{rot}}^{\perp}$ of $W_{x,\mathrm{rot}}$ with respect to K_x is then constituted by all $v \in T_x(Q)$ satisfying

$$K_x(v, R_\xi(x)) = (\Sigma m_k v_k \wedge x_k \mid \xi) = 0 , \tag{2.17}$$

where we have used (2.13). A. Guichardet defined the vibrational subspace $W_{x,\mathrm{vib}}$ as the orthogonal complement of $W_{x,\mathrm{rot}}$, so that one has

$$W_{x,\mathrm{vib}} = \{ v \in T_x(Q) \mid \Sigma m_k v_k \wedge x_k = 0 \} . \qquad (2.18)$$

This definition (2.18) is a geometric implication of the Eckart condition of rotationless constraint, though Eckart discussed small vibrations of molecules at equilibrium in his original paper [*1*].

Now the very definition of $W_{x,\mathrm{vib}}$ means that $T_x(Q)$ splits into an orthogonal direct sum;

$$T_x(Q) = W_{x,\mathrm{rot}} \oplus W_{x,\mathrm{vib}} . \qquad (2.19)$$

This decomposition gives a connection on the principal fiber bundle Q, which was defined by Guichardet. We mention here that, in the connection theory [*7*], $W_{x,\mathrm{rot}}$ and $W_{x,\mathrm{vib}}$ are referred to as vertical and horizontal subspaces, respectively.

2.3. **The connection and curvature forms.**

So far we have treated the connection in terms of vector fields. We turn to describing the connection in terms of differential forms. We start with the inertia operator A_x of the configuration x: A_x is the linear operator in $\Lambda^2\mathbf{R}^d$ defined by

$$A_x(\xi) = - \Sigma m_k x_k \wedge R_\xi(x_k). \qquad (2.20)$$

Note that the minus sign in (2.20) should be attributed to the definition of R. Using (2.14) and (2.1), we obtain

$$(\xi \mid A_x(\zeta)) = \Sigma m_k(R_\xi(x_k) \mid R_\zeta(x_k)) = K_x(R_\xi(x), R_\zeta(x)) , \qquad (2.21)$$

from which it follows that A_x is symmetric and positive definite. Furthermore, the mapping $x \to A_x$ is equivariant with respect to the action of $SO(d)$ on $\Lambda^2\mathbf{R}^d$, that is,

$$A_{gx} = g \circ A_x \circ g^{-1} . \qquad (2.22)$$

This is easily verified by using (2.12).

We now proceed to discuss the connection in terms of differential forms. The connection form ω on Q with values in $so(d)$ is defined in such a manner that for each $v \in T_x(Q)$, $\omega(v)$ equals a unique element R_ξ satisfying the condition that $R_\xi(x)$ is the rotational component of v [*7*].

The connection form is then written as

$$\omega_x(v) = R(- A_x^{-1}(\Sigma m_k x_k \wedge v_k)) , \qquad (2.23)$$

where we have written $R(\xi)$ instead of R_ξ for notational convenience.

By definition, $\omega(v)$ vanishes if and only if v is vibrational. The connection form is characterized by the properties [7]

$$i) \qquad \omega_x(\mathrm{R}_\xi(x)) = \mathrm{R}_\xi\,, \tag{2.24}$$

$$ii) \qquad \Phi_g^*\omega = \mathrm{Ad}_g\,\omega\,, \tag{2.25}$$

where Φ_g denote the action of g on Q; $\Phi_g(x) = gx$, and Φ_g^* its pull-back. The first is clear from (2.23). The second is proved by virtue of (2.12) and (2.22). We note here that in the usual definition of connections [7], Eq. (2.25) reads $\mathrm{R}_g^*\omega = \mathrm{Ad}_{g^{-1}}\omega$, where R_g is the right action, $\mathrm{R}_g(x) = xg$.

We turn to the curvature from Ω of ω, which is defined as the exterior covariant derivative of ω. The Ω is known to be given for $v, u \in \mathrm{T}_x(\mathrm{Q})$ by the structure equation

$$\Omega(v, u) = d\omega(v, u) - [\omega(v), \omega(u)]\,. \tag{2.26}$$

It is here to be noted that in [7] the structure equation is expressed as $\Omega = d\omega + \frac{1}{2}[\omega, \omega]$. The minus sign in the right-hand side of (2.26) results from the left action of the structure group. The factor 1/2 depends on the choice of the definition of the exterior product. We adopt the definition in [17].

For vibrational vector fields v and u, the structure equation (2.26) reads

$$\Omega(v, u) = -\,\omega([v, u])\,. \tag{2.27}$$

Writing out the bracket $[v, u]$, we obtain, for vibrational vector fields,

$$\Omega(v, u) = 2\mathrm{R}(-\,\mathrm{A}_x^{-1}(\Sigma m_k v_k \wedge u_k))\,. \tag{2.28}$$

This equation implies that the curvature never vanishes. In fact, A. Guichardet showed: for $x \in \mathrm{Q}$ such that $x_1, \ldots, x_\mathrm{N}$ generate $\mathbf{R}^d$ ($\mathrm{N} > d$), the elements $\Sigma m_k v_k \wedge u_k$ generate $\Lambda^2\mathbf{R}^d$ when v and u run over $\mathrm{W}_{x,\mathrm{vib}}$. In case of $\mathrm{N} = d$, those elements generate a proper subspace of $\Lambda^2\mathbf{R}^d$.

Furthermore, it follows from (2.28) that the vectors $\Omega(v, u)(x)$ span $\mathrm{W}_{x,\mathrm{rot}}$ when v and u run over $\mathrm{W}_{x,\mathrm{vib}}$ ($\mathrm{N} > d$). Using this fact, A. Guichardet was also able to show the non-separability of vibration from rotation for finite motions.

For the three-body system, the connection and curvature forms are given in an explicit form in [15-16].

3. THE ECKART FRAME

The problem we deal with in this section is this: Can one find a moving frame relative to which the molecule moves without rotations? Because of non-vanishing curvature, such a moving frame does not exist uniquely for any configuration, but does along any curve in Q. We have here to realize the difference between « uniquely for any configuration » and « along a curve of configurations ». Suppose we have two curves C_1 and C_2 in Q with the same initial and end points. We denote such a moving frame along C_1 and C_2 by R_1 and R_2, respectively. Then, even if R_1 and R_2 coincide at the initial point (it is possible), R_1 and R_2 does not coincide at the end point of the curves. This implies that such a moving frame cannot be found uniquely for any configuration.

3.1. **Parallel displacement.**

Let $x(t) = (x_1(t), \ldots, x_N(t))$ be a smooth curve in Q. We are inquiring the condition for a curve $g(t)$ in $SO(d)$ to give rise to a vibrational curve $y(t)$ in Q such that $x(t) = g(t)y(t)$. Here a vibrational curve $y(t)$ is a curve such that $\dot{y}(t)$ is a vibrational vector for all t. What we wish to perform is to express $\omega_{y(t)}(\dot{y}(t))$ in terms of $g(t)$ and $x(t)$. If it is accomplished, the condition inquired is given by $\omega_{y(t)}(\dot{y}(t)) = 0$.

Differentiated with respect to t, $x(t) = g(t)y(t)$ gives

$$\dot{x}_k = \dot{g}y_k + g\dot{y}_k\,. \tag{3.1}$$

Then we obtain, after a calculation,

$$\Sigma m_k x_k \wedge \dot{x}_k = g(\Sigma m_k y_k \wedge g^{-1}\dot{g}y_k + \Sigma m_k y_k \wedge \dot{y}_k)\,. \tag{3.2}$$

Setting $g^{-1}\dot{g} = R_\xi$, where ξ depending on t, and operating (3.2) with g^{-1}, $-A_y^{-1}$, and R in this order, we obtain

$$R(-A_y^{-1}g^{-1}(\Sigma m_k x_k \wedge \dot{x}_k)) = \omega_y(R_\xi(y)) + \omega_y(\dot{y}) = g^{-1}\dot{g} + \omega_y(\dot{y})\,. \tag{3.3}$$

Furthermore, we employ (2.22) with $x = gy$ to put (3.3) into

$$g^{-1}\omega_x(x)g = g^{-1}\dot{g} + \omega_y(\dot{y})\,. \tag{3.4}$$

From this it follows that a necessary and sufficient condition for $y(t) = g^{-1}(t)x(t)$ to be vibrational is given by

$$dg/dt = \omega_x(\dot{x})g\,. \tag{3.5}$$

This equation has a unique solution such that $g(0) = \mathrm{id}$. Hence $y(t)$ becomes vibrational for the given $x(t)$. The mapping $y(0) \to y(t)$ is called a parallel displacement [7].

3.2. **The Eckart frame.**

Let $x(t)$ be any smooth motion of a molecule. Let $g(t)$ remain to be a unique solution to (3.5) with $g(0) = \mathrm{id}$. Denoted by $f_1(t), \ldots, f_d(t)$, the column vectors of the $g(t)$ constitute a one-parameter family of orthonormal systems in $\mathbf{R}^d$ or a moving frame attached to the molecule. We now show that the molecule moves without rotation relative to the frame $\{ f_j(t) \}$.

Let r_k^j be the components of x_k with respect to the frame $\{ f_j(t) \}$;

$$x_k(t) = \Sigma f_j(t) r_k^j(t) . \tag{3.6}$$

If we mean the column vector of the components r_k^j, $j = 1, \ldots, d$, by r_k, the expression (3.6) takes a simple form; $x_k(t) = g(t) r_k(t)$. Then we can exploit the result in Sec. 3.1 to obtain

$$g^{-1} \omega_x(\dot{x}) g = g^{-1} \dot{g} + \omega_r(\dot{r}) , \tag{3.7}$$

where $r = (r_1, \ldots, r_N)$, an ennuple, and $\omega_r(\dot{r})$ is given by (2.23) with x_k's and v_k's replaced by r_k and $\dot{r}_k$, respectively. Since $g(t)$ is subject to (3.5), Eq. (3.7) yields $\omega_r(\dot{r}) = 0$, and therefore

$$\Sigma m_k r_k \wedge \dot{r}_k = 0 , \tag{3.8}$$

which means that the molecular motion is rotationless relative to the frame $\{ f_j(t) \}$. Hence we call the $\{ f_j(t) \}$ the Eckart frame.

In summary, we have shown:

Let $x(t) = (x_k(t))$ be any smooth curve in the center-of-mass system Q, and $\{ e_j \}$ a fixed frame in $\mathbf{R}^d$. A moving frame $f_j(t) = g(t) e_j$ is called an Eckart frame if $x(t)$ is rotationless relative to the frame $\{ f_j(t) \}$ or, equivalently, if the curve $g^{-1}(t) x(t)$ is vibrational. This condition implies that the curve $g(t)$ and therefore $\{ f_j(t) \}$ is uniquely determined by the curve $x(t)$.

However, as a consequence of the existence of a non-trivial holonomy, the value $f_j(t_0)$ for a fixed t_0 does not depend only on the value $x(t_0)$. This means the nonuniqueness of the Eckart frame.

The existence of a non-trivial holonomy is supported by the non-vanishing of the curvature. We approach again the nonuniqueness of the Eckart frame through the non-vanishing of the curvature form Ω. We will see in Sec. 4 how the curvature comes into molecular dynamics. Recalling that the ordinary differential equation (3.5) defines the Eckart frame along a curve of configurations, we turn to dealing with matrices g. If the contour integral $\int dg(t)$ were independent of a choice of $x(t)$, g would be a matrix-valued function on Q satisfying the exterior differential equation

$$dg = \omega g , \tag{3.9}$$

where ω is thought of as a matrix-valued differential form;

$$\omega = \mathrm{R}(- \mathrm{A}_x^{-1}(\Sigma m_k x_k \wedge dx_k)) . \tag{3.10}$$

Then g would be determined uniquely for any configuration $x \in \mathrm{Q}$. Now the integrability condition for (3.9) is given by

$$d^2 g = (d\omega - \omega \wedge \omega) g = 0 . \tag{3.11}$$

If this were satisfied, the structure equation (2.26), written in the matrix form,

$$\Omega = d\omega - \omega \wedge \omega, \tag{3.12}$$

would imply that $\Omega = 0$. However, this is a contradiction, because Ω does not always vanish, as was shown in Sec. 2.3. Thus the Eckart frame proves to depend on a choice of $x(t)$.

However, if we restrict $x(t)$ to vibrational curves only; $\Sigma m_k x_k \wedge \dot{x}_k = 0$, the Eckart frame is constant because of $\dot{g} = \omega_x(\dot{x})g = 0$, so that it is independent of vibrational curves.

4. REDUCTION OF THE PHASE SPACE

As we have shown in Sec. 3, the Eckart frame is not unique, so that it is not suitable for describing the internal molecular motions. We then choose to use the reduction method in Hamiltonian mechanics in order to get rid of rotations and translations from the molecular dynamics. To this end, we treat in this section linear and angular momentums in the Hamiltonian formalism, and thereby reduce the phase space $T^*(Q_0)$.

4.1. Hamiltonian formalism.

We start with momentum variables. Recall that the metric K is defined on Q_0 by (2.1). Then the cotangent space $T_x^*(Q_0)$ at $x \in Q_0$ is isomorphic with the tangent space $T_x(Q_0)$ by the induced isomorphism $K_x^\flat$ defined by

$$K_x^\flat(v) \cdot u = K_x(v, u) \qquad \text{for} \quad v, u \in T_x(Q_0), \tag{4.1}$$

where the dot means the pairing of covectors and vectors. Setting $p = K_x^\flat(v)$ and writing $p = (p_1, \ldots, p_N)$ as an ennuple, we have, from the definition of K_x,

$$p_k = m_k v_k, \tag{4.2}$$

$$p \cdot u = \Sigma(p_k \mid u_k). \tag{4.3}$$

Thus we obtain induced variables (x, p) constituting a coordinate system of $T^*(Q_0) \cong Q_0 \times (\mathbf{R}^d)^N$. The x and p are often called coordinate and momentum variables, respectively.

On the cotangent bundle $T^*(Q_0)$ there is defined a canonical one-form [12], denoted by θ. Let (u, w) be a tangent vector at $(x, p) \in T^*(Q_0)$. Then the θ is defined by

$$\theta_{(x,p)}(u, w) = p \cdot u. \tag{4.4}$$

If we let u be a vector field on Q_0, we have $dx_k^i(u) = u_k^i$ in the Cartesian coordinates, so that the canonical one-form θ is expressed in the form

$$\theta = p \cdot dx = \Sigma(p_k \mid dx_k). \tag{4.5}$$

The exterior derivative of θ is called the canonical two-form, having the form

$$d\theta = dp \wedge dx = \Sigma(dp_k \wedge dx_k), \tag{4.6}$$

where we have dropped the dot for the pairing and the vertical bar for the inner product.

On each cotangent space $T_x^*(Q_0)$, a natural scalar product K_x^* is defined for $q, p \in T_x^*(Q_0)$ by

$$K_x^*(q,p) = K_x(K_x^\#(q), K_x^\#(p)) = \Sigma(q_k \mid p_k)/m_k, \tag{4.7}$$

where $K_x^\# := (K_x^\flat)^{-1}$. The Hamiltonian of the molecule is then a function on $T^*(Q_0)$ of the form

$$H = K^*(p,p) + U, \tag{4.8}$$

where U is a potential function invariant under the translations $\mathbf{R}^n$ and the rotations $SO(d)$. Thus our Hamiltonian system is a triple $(T^*(Q_0), d\theta, H)$. Hamilton's equations of motion are then given through the Hamiltonian vector field X_H determined by $i(X_H)d\theta = -dH$, $i(X_H)$ indicating the interior product by X_H.

A transformation which leaves $d\theta$ invariant is called symplectic (or canonical). Let G be a group of symplectic transformations, and $\mathbf{G}$ its Lie algebra, identified with the tangent space to G at the identity. For $\alpha \in \mathbf{G}$ we mean a one-parameter subgroup of G by $\exp t\alpha$. Then its infinitesimal generator $\alpha_{P_0}(P_0 = T^*(Q_0))$ is defined by

$$\alpha_{P_0}(x,p) = \frac{d}{dt}(\exp t\alpha)(x,p)\,|_{t=0}\,. \tag{4.9}$$

If for any $\alpha \in \mathbf{G}$ there is a function F_α on $T^*(Q_0)$ satisfying

$$i(\alpha_{P_0})d\theta = -dF_\alpha, \tag{4.10}$$

the action of G is called strongly symplectic. If this is the case, the function F_α, depending linearly on α, is expressed in the form

$$F_\alpha(x,p) = J(x,p)\cdot\alpha, \tag{4.11}$$

where the dot means the pairing between $\mathbf{G}$ and $\mathbf{G}^*$, the dual space to $\mathbf{G}$. This equation defines a momentum mapping J of $T^*(Q_0)$ to $\mathbf{G}^*$ up to an additive constant in $\mathbf{G}^*$.

If the action of G is exactly symplectic, that is, G leaves θ invariant, the momentum mapping is given through

$$J(x,p)\cdot\alpha = \theta(\alpha_{P_0}). \tag{4.12}$$

This equation [*12*] can be easily verified by using a formula as to Lie derivatives; $L_Y = d \circ i(Y) + i(Y) \circ d$ for a vector field Y. The momentum mapping given by (4.12) covers linear and angular momentums, as will be shown later.

We now refer to reduction of dynamical systems with symmetry. Marsden and Weinstein [5] gave geometrical concept to what is happening in the elimination of variables by using a conservation law. The idea was also shown in Smale [18] and is explained in Abraham and Marsden [12] and Marsden [19] with several examples. The reduction theorem states:

Let P be a symplectic manifold with a symplectic form σ, and G a symplectic group acting on P, which also acts on the dual space $\mathbf{G}^*$ to the Lie algebra $\mathbf{G}$ of G through the coadjoint action. Let $J : P \to \mathbf{G}^*$ be an Ad*-equivariant momentum mapping associated with the action of G, that is, $J(gp) = \mathrm{Ad}^*_{g^{-1}}J(p)$ for all $p \in P$. Suppose for $\mu \in \mathbf{G}^*$, $J^{-1}(\mu)$ is a submanifold of P. Denote by G_μ an isotropy subgroup of G at $\mu \in \mathbf{G}^*$, so that, $\mathrm{Ad}^*_{g^{-1}}\mu = \mu$ for all $g \in G_\mu$. Suppose $P_\mu := J^{-1}(\mu)/G_\mu$ is a manifold with canonical projection $\pi_\mu : J^{-1}(\mu) \to P_\mu$. Then there is a unique symplectic form σ_μ on P_μ such that $\pi_\mu^*\sigma_\mu = \iota_\mu^*\sigma$, where $\iota_\mu : J^{-1}(\mu) \to P$ is the inclusion map, and therefore P_μ is called the reduced phase space. If a Hamiltonian H on P is invariant under the action of G, the Hamiltonian vector field X_H projects to a vector field on P_μ, namely, $\pi_{\mu *}X_H = X_{H_\mu}$ with $\pi_\mu^*H_\mu = \iota_\mu^*H$.

4.2. Linear momentum.

Though the reduction by the linear momentum is elementary, we describe it for a comparison with the reduction by the angular momentum.

For the linear momentum, the translation group $\mathbf{R}^d$ plays the role of exact symplectic group. In effect, the action of $\mathbf{R}^d$ on $T^*(Q_0)$ defined for $a \in \mathbf{R}^d$ by

$$(x_k, p_k) \to (x_k + a, p_k) \tag{4.13}$$

leaves invariant the canonical one-form θ given by (4.5). For $\gamma \in \mathbf{R}^d$, $\mathbf{R}^d$ denoting the Lie algebra of the translation group, the infinitesimal generator of $a(t) = t\gamma$ have the form

$$\gamma_{P_0}(x, p) = (\gamma, \ldots, \gamma, 0, \ldots, 0), \qquad (P_0 = T^*(Q_0)) \tag{4.14}$$

so that the momentum mapping J_t of $T^*(Q_0)$ to $\mathbf{R}^d$ is given from (4.12) in the form

$$J_t(x, p) \cdot \gamma = \theta(\gamma_{P_0}) = \Sigma(p_k \mid \gamma) = (\Sigma p_k \mid \gamma). \tag{4.15}$$

Thus we obtain the usual linear momentum

$$J_t(x, p) = \Sigma p_k , \tag{4.16}$$

where we have identified the dual space to the Lie algebra $\mathbf{R}^d$ with $\mathbf{R}^d$ itself by the inner product (|).

We now apply the reduction theorem for the translation group $\mathbf{R}^d$ acting on $T^*(Q_0)$. The Ad*-equivariance of J_t is clear, since J_t is $\mathbf{R}^d$-invariant, and since Ad* equals the identity because $\mathbf{R}^d$ is abelian. Let $\lambda \in \mathbf{R}^d$. Then $J_t^{-1}(\lambda)$ is a submanifold of $T^*(Q_0)$ determined by $\Sigma p_k = \lambda$. The isotropy subgroup at λ is $\mathbf{R}^d$ itself, as $\mathbf{R}^d$ is abelian. Hence $J_t^{-1}(\lambda)$ is diffeomorphic with $Q_0 \times (\mathbf{R}^d)^{N-1}$ for any λ, and the reduced phase space $J_t^{-1}(\lambda)/\mathbf{R}^d$ can be identified with $(Q_0/\mathbf{R}^d) \times (\mathbf{R}^d)^{N-1}$ and therefore with $Q \times (\mathbf{R}^d)^{N-1}$. Thus $J_t^{-1}(\lambda)/\mathbf{R}^d$ is realized as a submanifold of $T^*(Q_0)$ determined by $\Sigma m_k x_k = 0$ and $\Sigma p_k = \lambda$. We are interested in $J_t^{-1}(0)/\mathbf{R}^d$ realized by the condition

$$\Sigma m_k x_k = 0\,, \qquad \Sigma p_k = 0. \tag{4.17}$$

The submanifold determined by (4.17) can be identified with the cotangent bundle $T^*(Q)$ of the center-of-mass system Q. The reduced symplectic form on $T^*(Q)$ is now the restriction of $d\theta$ on $T^*(Q)$. The reduced Hamiltonian on $T^*(Q)$ is also the restriction of H on $T^*(Q)$. For notational convenience, we denote them by the same letters as those on $T^*(Q_0)$; $d\theta$ and H subject to the condition (4.17).

4.3. **Angular momentum.**

We now proceed to the angular momentum defined on $T^*(Q)$. The rotation group $SO(d)$ plays in turn the role of an exact symplectic group, whose action on $T^*(Q)$ is defined for (x,p) and $g \in SO(d)$ by

$$(x,p) \rightarrow (gx, gp)\,. \tag{4.18}$$

We note here that $SO(d)$ acts actually on $T^*(Q)$ as the conditions (4.17) are invariant under $SO(d)$, and also that if (p_k) are subject to $\Sigma p_k = \lambda \neq 0$, only a subgroup of $SO(d)$ acts on $J_t^{-1}(\lambda)/\mathbf{R}^d$. It is now an easy matter to check that $SO(d)$ leaves θ invariant. It is also easy to see that for $\alpha = R_\xi \in so(d)$ the infinitesimal generator of $\exp t\alpha$ is given by

$$\alpha_P(x,p) = (R_\xi(x), R_\xi(p))\,. \qquad (P = T^*(Q)) \tag{4.19}$$

Therefore, we obtain from (4.12) the momentum mapping J_r of $T^*(Q)$ to $so(d)^*$, the dual space to $so(d)$, as follows:

$$\begin{aligned} J_r(x,p)\cdot\alpha &= \theta(\alpha_P) = \Sigma(p_k \mid R_\xi(x_k)) \\ &= (\Sigma p_k \wedge x_k \mid \xi) = (R(\Sigma p_k \wedge x_k) \mid R_\xi)\,, \end{aligned} \tag{4.20}$$

hence

$$J_r(x,p) = R(-\,\Sigma x_k \wedge p_k)\,. \tag{4.21}$$

Here we have used (2.10) and (2.13), and identified $so(d)^*$ with $so(d)$ through the scalar product on $so(d)$ (see (2.9)). The minus sign in (4.21) is to be attributed to the definition of R.

We remark here that J_r is Ad*-equivariant. While this is a specialization of the theorem [*12*] that for an exact symplectic group the associated momentum mapping is Ad*-equivariant, we give a short proof; from (2.12) and (4.21) one has

$$J_r(gx, gp) = gJ_r(x,p)g^{-1}\,. \tag{4.22}$$

We here note that since $so(d)^*$ is identified with $so(d)$ the Ad*-equivariance is expressed in the form of adjoint equivariance.

We are now in a position to apply the reduction theorem for the rotation group $SO(d)$. Let $\mu \in so(d) \cong so(d)^*$. Then $J_r^{-1}(\mu)$ is a submanifold of $T^*(Q)$. Factoring out the orbits of the isotropy subgroup G_μ of $SO(d)$ at μ, we obtain a reduced phase $J_r^{-1}(\mu)/G_\mu$. This process is nothing but the elimination of the angular momentum. A question now arises as to whether or not the reduced phase space is diffeomorphic to the cotangent bundle $T^*(M)$ of the internal space M defined in Sec. 2.1. However, unlike the result for the translation group, the answer is « no » if $\mu \neq 0$ and $d \geqq 3$. For a reason, we invoke Jacobi's celebrated « elimination of the nodes ». According to Wintner [*20*], for the N-body problem in $\mathbf{R}^3$ ($d = 3$), the dimensions of the Hamiltonian system reduce by $3 + 1 = 4$ by eliminating the angular momentum. The number 4 is accounted for as follows: For $d = 3$, $\dim so(d) = 3$, and the isotropy subgroup G_μ turns out to be $SO(2)$, so that the condition $J_r = \mu$ diminishes dimensions by three and the factoring out of $SO(2)$ orbits does by one. On the other hand, $\dim T^*(M)$ is less than $\dim T^*(Q)$ by $3 \times 2 = 6$. From this it follows that $\dim J_r^{-1}(\mu)/G_\mu > \dim T^*(M)$. This is the case in general. Because for $d \geqq 3$, the total group $SO(d)$ is an isotropy subgroup G_μ if and only if $\mu = 0$.

However, if $\mu = 0$, that is, the angular momentum vanishes, the isotropy subgroup at 0 is $SO(d)$ itself, so that we can expect that the reduced phase space $J_r^{-1}(0)/SO(d)$ should be $T^*(M)$. To show that this is the case, we employ Kummer's theorem [*21*], which says:

Let $Q \to M$ be a principal G-bundle. Let $J: T^*(Q) \to \mathbf{G}^*$ be an Ad*-equivariant momentum mapping, where the action of G is lifted on $T^*(M)$ so as to be exact symplectic. Suppose $\mu \in \mathbf{G}^*$ be G-invariant. Then each connection ω on the G-bundle defines a symplectomorphism between the reduced phase space $P_\mu = J^{-1}(\mu)/G$ and the cotangent bundle $T^*(M)$, the latter being endowed with a symplectic form consisting of the canonical symplectic form on $T^*(M)$ plus the μ-component of the curvature of the connection ω, viewed as a two-form on M. (See also Montgomery [*22*].)

Applying this theorem in our case, we have a symplectomorphism of $J_r^{-1}(0)/SO(d)$ to $T^*(M)$ together with the reduced symplectic form σ_0 ($\mu = 0$) equal to the canonical symplectic form on $T^*(M)$. We note here that $J_r^{-1}(0)$ is a submanifold because the point $x = 0$ is got rid of. See Bos and Gotay [*23*].

Without use of Kummer's theorem, we can attain $T^*(M)$ in a conceptual manner. From (4.21) the condition $J_r = 0$ is equivalent to $\Sigma x_k \wedge p_k = 0$. This equation defines, at every point x of Q, the subspace of the cotangent space $T_x^*(Q)$ which is the dual space to $W_{x,\text{vib}} \cong T_{\pi(x)}(M)$;

$$W_{x,\text{vib}}^* = \{ p \in T_x^*(Q) \mid \Sigma x_k \wedge p_k = 0 \} . \tag{4.23}$$

Thus we see that the submanifold $J_r^{-1}(0)$ consists of all the points (x, p)

subject to $x \in \mathrm{Q}$ and $p \in \mathrm{W}^*_{x,\mathrm{vib}} \cong \mathrm{T}^*_{\pi(x)}(\mathrm{M})$. The rotation group acts on $\mathrm{J}_r^{-1}(0)$, since the condition $\Sigma x_k \wedge p_k = 0$ is invariant under $\mathrm{SO}(d)$. Consequently, the orbit space $\mathrm{J}_r^{-1}(0)/\mathrm{SO}(d)$ turns out to be the cotangent bundle of $\mathrm{Q}/\mathrm{SO}(d) = \mathrm{M}$.

There is another case in which the reduced phase space $\mathrm{J}_r^{-1}(\mu)/\mathrm{G}_\mu$ is diffeomorphic with $\mathrm{T}^*(\mathrm{M})$. In fact, if $d = 2$, the isotropy subgroup G_μ is just equal to $\mathrm{SO}(d)$, so that Kummer's theorem gives a desired diffeomorphism. Kummer's symplectomorphism of $\mathrm{J}_r^{-1}(\mu)/\mathrm{SO}(2)$ with $\mathrm{T}^*(\mathrm{M})$ will be pointed out in the last paragraph of this section. Topology of the planar N-body problem was studied in Smale [*24*].

In conclusion we wish to study the symplectic form σ_μ on the reduced phase space $\mathrm{J}_r^{-1}(\mu)/\mathrm{G}_\mu$ for $\mu \neq 0$. Since σ_μ is defined by $\pi_\mu^*\sigma_\mu = \iota_\mu^*\sigma$, and since $\sigma = d\theta$ in our case, we have only to consider $\iota_\mu^* d\theta = d(\iota_\mu^*\theta)$. In what follows, we work on $\mathrm{T}(\mathrm{Q})$ for notational convenience, as $\mathrm{T}(\mathrm{Q})$ can be endowed with a canonical symplectic form, denoted by the same letter as that on $\mathrm{T}^*(\mathrm{Q})$, through the isomorphism of $\mathrm{T}(\mathrm{Q})$ to $\mathrm{T}^*(\mathrm{Q})$;

$$\theta = \Sigma m_k(v_k \mid dx_k) = \mathrm{K}(v, dx). \tag{4.24}$$

We first define a map $\omega_x^* : \mathrm{so}(d) \to \mathrm{T}_x(\mathrm{Q})$ dual to $\omega_x : \mathrm{T}_x(\mathrm{Q}) \to \mathrm{so}(d)$, where we have taken $\mathrm{so}(d) \simeq \mathrm{so}(d)^*$ and $\mathrm{T}_x(\mathrm{Q}) \cong \mathrm{T}_x^*(\mathrm{Q})$ into account. For $\alpha \in \mathrm{so}(d)$ and $v \in \mathrm{T}_x(\mathrm{Q})$, ω_x^* is defined actually by

$$(\omega_x(v) \mid \alpha) = \mathrm{K}_x(v, \omega_x^*(\alpha)). \tag{4.25}$$

Using the ω_x^*, we show that for any $v \in \mathrm{T}_x(\mathrm{Q})$ the vector $v - \omega_x^*\mathrm{J}_r(x,p)$ with $\mathrm{K}_x^\#(p) = v$ is vibrational. To this end, it is sufficient to prove that $v - \omega_x^*\mathrm{J}_r(x,p)$ and $\mathrm{R}_\xi(x)$ are orthogonal for any $\xi \in \Lambda^2\mathbf{R}^d$;

$$\begin{aligned}
&\mathrm{K}_x(\mathrm{R}_\xi(x), v - \omega_x^*\mathrm{J}_r(x,p)) \\
&\qquad = \mathrm{K}_x(\mathrm{R}_\xi(x), v) - \mathrm{K}_x(\mathrm{R}_\xi(x), \omega_x^*\mathrm{J}_r(x,p)) \\
&\qquad = \Sigma m_k(\mathrm{R}_\xi(x_k) \mid v_k) - (\omega_x(\mathrm{R}_\xi(x)) \mid \mathrm{J}_r(x,p)) \\
&\qquad = (\xi \mid \Sigma m_k v_k \wedge x_k) - (\mathrm{R}_\xi \mid \mathrm{R}(-\Sigma x_k \wedge p_k)) \\
&\qquad = -(\xi \mid \Sigma x_k \wedge m_k v_k) + (\xi \mid \Sigma x_k \wedge p_k) = 0.
\end{aligned} \tag{4.26}$$

On thinking of (x, v) as a coordinate system in $\mathrm{T}(\mathrm{Q})$, the submanifold $\mathrm{J}_r^{-1}(\mu)$ is determined in $\mathrm{T}(\mathrm{Q}) \simeq \mathrm{T}^*(\mathrm{Q})$ by the condition $\mathrm{R}(-\Sigma m_k x_k \wedge v_k) = \mu$. Let

$$w = v - \omega_x^*\mathrm{J}_r(x,p) \qquad \text{with} \qquad \mathrm{K}_x^\#(p) = v. \tag{4.27}$$

Then the pair (x, w) meets the condition $\mathrm{R}(-\Sigma m_k x_k \wedge w_k) = 0$, so that it serves as a coordinate system in $\mathrm{J}_r^{-1}(0)$ under that condition. A coordinate system on $\mathrm{J}_r^{-1}(\mu)$ then can be given by the pair $(x, w + \omega_x^*\mu)$.

With this in mind we rewrite the canonical one-form θ;

$$\begin{aligned}
\theta &= \mathrm{K}_x(w, dx) + \mathrm{K}_x(\omega_x^*\mathrm{J}_r(x,p), dx). \\
&= \mathrm{K}_x(w, dx) + (\mathrm{J}_r(x,p) \mid \omega_x \circ dx).
\end{aligned} \tag{4.28}$$

Consequently, on $J_r^{-1}(\mu)$ we have

$$(\iota_\mu^*\theta)_{(x,v)} = K_x(w, dx) + (\mu \mid \omega_x \circ dx), \tag{4.29}$$

where $v = w + \omega_x^*\mu$. Thus the canonical two-form $d\theta$ restricts to $d(\iota_\mu^*\theta)$ on $J_r^{-1}(\mu)$;

$$d\iota_\mu^*\theta = d(K(w, dx)) + d(\mu \mid \omega), \tag{4.30}$$

where ω is the matrix-valued one-form given by (3.10). As is easily seen, the right-hand side of (4.30) is G_μ-invariant, and so is the left-hand side: $\Phi_g^* d\iota_\mu^*\theta = d\iota_\mu^*\theta$ for $g \in G_\mu$. Therefore, $d\iota_\mu^*\theta$ projects to a symplectic form on $J_r^{-1}(\mu)/G_\mu : \pi_\mu^*\sigma_\mu = d\iota_\mu^*\theta$.

We now look into each term in (4.30). Since w is vibrational; $w \in W_{x,\mathrm{vib}} \cong T_{\pi(x)}(M)$, the first term in the right-hand side of (4.30), invariant under $SO(d)$, is in one-to-one correspondence with the canonical two-form on $T(M) \cong T^*(M)$. Contrary to this, the second term of the same side, depending only on x, cannot project to a two-form on M. In fact $(\mu \mid d\omega)$ is not vibrational (or horizontal); we have to recall that the horizontal part of $d\omega$ is defined as the curvature form [*7*]. The term $(\mu \mid d\omega)$, when projected on the reduced phase space, serves as an external field, to which we may attribute the Coriolis force. If $d = 2$, the two-form $(\mu \mid d\omega)$, invariant under $SO(2)$, will define a « magnetic field » on M. In fact, in this case, the form equals $(\mu \mid \Omega)$, where Ω is the curvature form. Hence it is vibrational, and therefore can project to a two-form on M, which is thought of as a magnetic 2-form. Indeed, the form (4.30) is reminiscent of a symplectic form which is used in a description of the charged particle motion in a magnetic field [*13*]. We conclude this section by remarking that $(\mu \mid \Omega)$ is the μ-component of the curvature in Kummer's theorem. Thus we come to Kummer's symplectomorphism in the case of $d = 2$.

5. REDUCTION OF THE HAMILTONIAN

This section shows that the kinetic energy of a molecule separates into vibrational and rotational energies. We treat the kinetic energy in the tangent bundle T(Q), as we have done in Sec. 4.3 for the symplectic form (see (4.24)). Recall the decomposition (2.19) and denote by P_x the orthogonal projection: $T_x(Q) \to W_{x,\mathrm{rot}}$. Set $H_x = 1_x - P_x$, where 1_x denotes the identity in $T_x(Q)$. From the definition of the connection, one has

$$\omega_x(v)(x) = P_x(v), \tag{5.1}$$

where we notice that ω_x is a mapping of $T_x(Q)$ to $so(d)$. Then any tangent vector v at x is broken up into the orthogonal sum

$$v = P_x(v) + H_x(v), \tag{5.2}$$

so that one has, for $v, u \in T_x(Q)$,

$$K_x(v, u) = K_x(P_x(v), P_x(u)) + K_x(H_x(v), H_x(u)). \tag{5.3}$$

If we set $v = u$ in (5.3), we obtain the kinetic energy expressed as the sum of rotational and vibrational energies. No Coriolis energy appears. However, this does not mean that the coupling between rotation and vibration disappears. The coupling rather comes into dynamics through the connection form ω (see (4.30)).

5.1. **Vibrational energy.**

We first pick out the vibrational energy or the second term in the right-hand side of (5.3). We use again π as the natural projection of Q onto M. Then the tangent map π_* restricted on $W_{x,\mathrm{vib}}$ gives an isomorphism of $W_{x,\mathrm{vib}}$ with $T_{\pi(x)}(M)$. Let X and Y be tangent vectors in $T_m(M)$, $m \in M$. Then at every point x with $\pi(x) = m$ one has unique vibrational vectors v and u satisfying $\pi_*(v) = X$ and $\pi_*(u) = Y$. Consequently, the vibrational energy or the second term in the right-hand side of (5.3) induces a Riemannian metric B on M through

$$B_m(X, Y) = K_x(v, u). \tag{5.4}$$

It is easy to verify that the definition (5.4) is independent of the choice of x with $\pi(x) = m$. In fact, for any $u, v \in W_{x,\mathrm{vib}}$ one has $\pi_*(gv) = X$, $\pi_*(gu) = Y$, and

$$K_{gx}(gv, gu) = K_x(v, u). \tag{5.5}$$

We notice here that the Riemannian metric B on M is a generalization of Wilson's G matrix [*14*].

We remark in conclusion upon the restriction of the vibrational energy to the submanifold $J_r^{-1}(\mu)$. By using the w defined by (4.27), the vibrational energy is written as $\frac{1}{2}K_x(w, w)$ with $R(-\Sigma m_k x_k \wedge w_k) = 0$, and is in one-to-one correspondence with the kinetic energy of the internal motion group (5.3).

5.2. **Rotational energy.**

We turn to the rotational energy or the first term in the right-hand side of (5.3). Using the definition of P_x, A_x, R, ω_x, and of the inner product on $\Lambda^2\mathbf{R}^d$ and $\mathrm{so}(d)$, we obtain

$$\begin{aligned}
K_x(P_x(v), P_x(u)) \\
&= K_x(\omega_x(v)(x), \omega_x(u)(x)) \\
&= \left(-A_x^{-1}(\Sigma m_k x_k \wedge v_k) \,\middle|\, A_x A_x^{-1}(-\Sigma m_k x_k \wedge u_k)\right) \\
&= \left(R(-A_x^{-1}(\Sigma m_k x_k \wedge v_k)) \,\middle|\, R A_x R^{-1} R A_x^{-1}(-\Sigma m_k x_k \wedge u_k)\right) \\
&= (\omega_x(v) \mid R A_x R^{-1} \omega_x(u)).
\end{aligned} \tag{5.6}$$

Here we notice that the symbol RA_xR^{-1} denotes the matrix of the operator A_x. In fact, on setting

$$A_x(e_i \wedge e_j) = \sum_{k<l} A_{kl,ij} e_k \wedge e_l, \tag{5.7}$$

one obtains, for an antisymmetric matrix $\alpha = (\alpha_{ij})$ and $x = (x^i) \in \mathbf{R}^d$,

$$(RA_xR^{-1}(\alpha))x = \sum_k \Big(\sum_l \Big(\sum_{i<j} A_{kl,ij}\alpha_{ij} \Big) x^l \Big) e_k . \tag{5.8}$$

Thus we know that the rotational energy is quadratic in the components of the connection $\omega_x(v)$.

We proceed to describe the rotational energy in terms of covectors. An easy way to do so is to substitute p_k for $m_k v_k$ in (5.6). The result is this;

$$\begin{aligned} K_x(P_x(v), P_x(v)) &= \big(-A_x^{-1}(\Sigma x_k \wedge p_k) \,\big|\, -\Sigma x_k \wedge p_k\big) \\ &= \big(RA_x^{-1}R^{-1}R(-\Sigma x_k \wedge p_k) \,\big|\, R(-\Sigma x_k \wedge p_k)\big) \\ &= \big(RA_x^{-1}R^{-1}J_r(x,p) \,\big|\, J_r(x,p)\big) . \end{aligned} \tag{5.9}$$

Here we have used (4.21), and notice that Eqs. (5.6) and (5.9) are in marked contrast.

If we take the conservation of the angular momentum, $J_r = \mu$, into account, the last expression in (5.9) becomes a function of x; $(RA_x^{-1}R^{-1}\mu \,|\, \mu)$. This function proves to be invariant under G_μ, and hence projects to a function on the reduced phase space, which serves in turn as a centrifugal potential for molecular motions.

6. THE REDUCED HAMILTONIAN SYSTEM

So far we have discussed the reduced phase space in Sec. 4 and the reduced kinetic energy in Sec. 5. We now put the results together. The reduced phase space $J_r^{-1}(\mu)/G_\mu$ carries the symplectic form σ_μ which are related to the canonical form $d\theta$ by $\iota_\mu^* d\theta = \pi_\mu^* \sigma_\mu$. On $J_r^{-1}(\mu)/G_\mu$ the reduced Hamiltonian H_μ is defined by $H_\mu \circ \pi_\mu = H \circ \iota_\mu$. These form and Hamiltonian are expressed, in the coordinate system (x, v) on $J_r^{-1}(\mu)$ with $v = w + \omega_x^* \mu$, as

$$\pi_\mu^* \sigma_\mu = \iota_\mu^* d\theta = d(K(w, dx)) + d(\mu \,|\, \omega), \tag{6.1}$$

$$H_\mu \circ \pi_\mu = H \circ \iota_\mu = \frac{1}{2} K(w, w) + \frac{1}{2} (RA_x^{-1}R^{-1}\mu \,|\, \mu) + U, \tag{6.2}$$

where $R(-\Sigma m_k x_k \wedge w_k) = 0$. The right-hand sides of (6.1) and (6.2) are invariant under G_μ, and hence thought of as quantities on the reduced phase space. Especially, the second term of the right-hand side of (6.1) is to be attributed to the source of the Coriolis force, and the middle term in the right-hand side of (6.2) is understood as a centrifugal potential. The first terms of (6.1) and (6.2) are in one-to-one correspondence with the canonical two-form and with the kinetic energy on $T^*(M) \cong T(M)$, respectively.

If $\mu = 0$, the reduced phase space is diffeomorphic to the cotangent bundle $T^*(M)$ of the internal space M, and the symplectic form σ_μ becomes the canonical one on $T^*(M)$. The reduced Hamiltonian H_μ is then a sum of the kinetic energy of internal motions and the potential on M. If $d = 2$ and $\mu \neq 0$, the reduced phase space is also diffeomorphic to $T^*(M)$, but the symplectic form σ_μ is the canonical one plus a two-form viewed as a « magnetic field » on M. The reduced Hamiltonian H_μ becomes the kinetic and potential energies plus a centrifugal potential. In these cases, the molecular motion is internal, that is, it can be described on $T^*(M)$ or in terms of internal coordinates and their conjugate momenta.

However, if $\mu \neq 0$ and $d \geqq 3$, the reduced phase space is larger than $T^*(M)$, so that the molecular motion cannot be considered as internal. For $d = 3$, we can picture that the molecule moves in response to the magnetic-like field $(\mu \mid d\omega)$, depending on its relative attitude to a fixed vector μ in $\mathbf{R}^3$. This result is characteristic of classical mechanics.

In quantum mechanics, however, the molecular motion is internal even if the angular momentum eigenvalue is not zero; that is, the internal states of the molecule are described as cross sections in a complex vector bundle over the internal manifold M, and the internal Hamiltonian operator is expressed as an operator acting on the space of cross sections. These results are published in [*15*] and [*16*]. See also Tachibana and Iwai [*25*] for quantum molecular dynamics.

ACKNOWLEDGEMENT

The author would like to thank Dr. A. Tachibana at Kyoto University for suggesting the problem and for much helpful discussion. He is also grateful to Prof. A. Guichardet and a referee for suggestive comments. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education in Japan.

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(Manuscrit reçu le 20 mars 1987)