Holonomy-reduced dynamics of triatomic molecules

Ünver Çiftçi[1] and Holger Waalkens[2]

[1] Department of Mathematics, Namık Kemal University, 59030 Tekirdağ, Turkey
[2] Johann Bernoulli Institute for Mathematics and Computer Science, University of Groningen, PO Box 407, 9700 AK Groningen, The Netherlands

E-mail: uciftci@nku.edu.tr and h.waalkens@rug.nl

Abstract

Whereas it is easy to reduce the translational symmetry of a molecular system using, e.g., Jacobi coordinates, the situation is much more involved for rotational symmetry. In this paper, we address the latter problem using *holonomy reduction*. We suggest that the configuration space may be considered as the reduced holonomy bundle with a connection induced by the mechanical connection. Using the fact that for the special case of the three-body problem the holonomy group is $SO(2)$ (as opposed to $SO(3)$ like in systems with more than three bodies), we obtain a holonomy-reduced configuration space of topology $\mathbf{R}_+^3 \times S^1$. The dynamics then takes place on the cotangent bundle over the holonomy-reduced configuration space. On this phase space, there is an S^1 symmetry action coming from the conserved reduced angular momentum which can be reduced using the standard symplectic reduction method. Using a theorem by Arnold it follows that the resulting symmetry-reduced phase space is again a natural mechanical phase space, i.e. a cotangent bundle. This is different from what is obtained from the usual approach where symplectic reduction is used from the outset. This difference is discussed in some detail, and a connection between the reduced dynamics of a triatomic molecule and the motion of a charged particle in a magnetic field is established.

PACS numbers: 45.50.Jf, 02.40.−k, 45.20.Jj
Mathematics Subject Classification: 70F07, 70G65, 53C80

1. Introduction

In molecular dynamics, which is the subject of this paper, and generally in dynamical systems theory, the reduction of the number of degrees of freedoms is of central importance for both computational and conceptual reasons. A molecular system is a many body system consisting of the nuclei and electrons of the constituting atoms. The electronic degrees of freedom are

typically dealt with in a Born–Oppenheimer approximation. Since the nuclear masses are a few thousands times bigger than the mass of an electron, one assumes that the nuclei adiabatically interact via the forces obtained from a potential energy surface that is obtained from the electronic ground state energy as a function of the nuclear configurations. The computation of such potential energy surfaces is based on density functional theory and other methods and is an art in physical chemistry. For several molecular systems, such potential energy surfaces are tabulated in the chemistry literature. Given such a potential energy surface, a molecular system reduces to an N-body system which only involves the degrees of freedom of the N nuclei in the system. This N-body system can then be treated classically or quantum mechanically. In particular, for light atoms (respectively nuclei) like hydrogen, quantum effects might play an important role which make a quantum mechanical treatment necessary. We note that state of the art quantum computations for, e.g., reactive scattering are even today only feasible for three or maximally four atoms. For this reason and also conceptual reasons one desires to get rid of as many degrees as possible. A reduction of the number of 'effective' degrees of freedom of a molecular N-body system can be achieved by exploiting the symmetries of the system. These symmetries consist of overall translations and rotations. The reduction of translational degrees of freedom is simple and can be achieved using Jacobi coordinates or changing to a centre of mass coordinate system. For rotations, the situation is much more involved as a clear distinction between rotational degrees of freedom and (internal) vibrational degrees of freedom only exists in an approximate sense in the vicinity of an equilibrium position. Here, the distinction between vibrations and rotations can be achieved from the so-called *Eckart frame* [1] that is widely used in applications [2]. This approximation is however only of local validity since large amplitude vibrations may produce rotations. A major step towards a geometric understanding of why a separation of rotations and vibrations cannot be achieved globally goes back to the work of Guichardet [3], who used the differential geometry framework of principal bundles to give a mathematically rigorous definition of vibrational motions. He showed that the translation-reduced configuration space is a principal bundle with the structure group given by the special orthogonal group, and introduced a connection which naturally relates to molecular motions. The inseparability of rotations and vibrations then follows from the nonvanishing curvature of this so-called *mechanical connection*. Iwai and Tachibana [4, 5] used Guichardet's approach to study in great detail both the classical and quantum mechanical dynamics of N-body molecular systems. Using the setting of principal bundles, Iwai [6] in particular showed that the Eckart frame can also be defined for general configurations (i.e. no necessarily equilibrium configurations) of a molecule. However, this frame is then not unique and therefore not suitable for studying large amplitude vibrational motions of a molecule. Iwai moreover applied the Marsden–Weinstein–Meyer symplectic reduction procedure [7, 8] to reduce the constant angular momentum motion of an N-body system. He showed that for nonvanishing angular momentum, the reduced phase space is then no longer a natural mechanical system in the sense that it is no longer given as the cotangent bundle over a (reduced) configuration space. A gauge theoretical interpretation of the reduction of symmetries and the related choice of a reference frame in N-body systems was introduced in [9, 10]. In their constructive and instructive paper, Littlejohn and Reinsch [10] used a gauge-invariant method instead of the symplectic reduction mentioned above. For more related work, we refer to [11–16].

In this paper, we use modern tools from the above-mentioned geometric description of molecular motion to introduce a new way to reduce the symmetry of triatomic molecular system. We obtain a reduced configuration space and deduce the reduced dynamics for a triatomic molecule in a way which can be summarized as follows. Consider three atoms (or nuclei) in $\mathbf{R}^3$. Using Jacobi coordinates, the translational symmetry in the absence of external

forces can be used to reduce the nine-dimensional configuration space $\mathbf{R}^3 \times \mathbf{R}^3 \times \mathbf{R}^3$ of the triatomic system to the six-dimensional space $\mathbf{R}^3 \times \mathbf{R}^3$. Excluding collinear (and hence also collisional) configurations from $\mathbf{R}^3 \times \mathbf{R}^3$ gives the translation-reduced configuration space P on which the special orthogonal group $SO(3)$ acts freely. The space P is a principal bundle with base space given by the positive half space $\mathbf{R}_+^3$ [11]. Kinetic energy gives a metric on P, and a connection can be obtained by defining horizontal spaces as orthogonal complements of the tangent spaces of orbits of the $SO(3)$ action. As known [3, 10], the connection on P has a nontrivial holonomy group which is $SO(2)$. This enables us to use the holonomy reduction theorem [17] to reduce P to the holonomy bundle which we denote by Q. Since P is a trivial bundle [11], Q is also trivial and hence topologically $\mathbf{R}_+^3 \times SO(2)$, or equivalently $\mathbf{R}_+^3 \times S^1$. The reduced phase space is then given by the cotangent bundle T^*Q. We explicitly derive the Hamiltonian on T^*Q and deduce the reduced dynamics on T^*Q. In the final step, we then use the conservation of the reduced angular momentum related to an S^1 action on T^*Q to apply the symplectic reduction procedure. Using a theorem in [18], we find that the reduced phase space is then a natural mechanical system, namely the cotangent bundle over Q/S^1.

We note that there is no natural way to generalize these results to systems of four or more atoms. The reason is that triatomic systems are in many respects special. For example, the holonomy group of a system of four or more atoms is $SO(3)$, and the translation-reduced space is not a trivial bundle [10].

2. Reduced configuration space

2.1. Principle bundle picture

Consider a molecular system of three atoms. Let $\mathbf{x}_i \in \mathbf{R}$, $i = 1, 2, 3$, be the position vectors of these atoms. Suppose that there are no external forces. Then the mass-weighted Jacobi vectors

$$\mathbf{r} = \sqrt{\frac{m_1 m_3}{m_1 + m_3}} (\mathbf{x}_1 - \mathbf{x}_3),$$

$$\mathbf{s} = \sqrt{\frac{m_2(m_1 + m_2)}{m_1 + m_2 + m_3}} \left(\mathbf{x}_2 - \frac{m_1 \mathbf{x}_1 + m_3 \mathbf{x}_3}{m_1 + m_3} \right)$$

can be chosen to reduce the symmetry of overall translations. (For different choices of Jacobi vectors, see appendix B.) Excluding collinear (and hence also collisional) configurations we obtain the six-dimensional translation-reduced configuration space

$$P = \left\{ x = (\mathbf{r}, \mathbf{s}) : \lambda \mathbf{r} + \mu \mathbf{s} \neq 0 \text{ for all } (\lambda, \mu) \in \mathbf{R}^2 \backslash \{0\} \right\} \subset \mathbf{R}^3 \times \mathbf{R}^3.$$

Proper rotations $g \in SO(3)$ act on P in the natural way:

$$g(\mathbf{r}, \mathbf{s}) = (g\mathbf{r}, g\mathbf{s}).$$

On P this action is free and it thus follows from standard results that

$$M := P/SO(3)$$

has a manifold structure. The space M is usually referred to as *shape space* or *internal space*. Furthermore, the canonical projection $\pi : P \to M$ defines a principal bundle with the structure group $SO(3)$ [3]. This means that P consists of smoothly glued copies of $SO(3)$, i.e. locally, P is diffeomorphic to $M \times SO(3)$. Topologically, this local decomposition also holds globally, which following Iwai [11] can be seen as follows. Using Jacobi coordinates

$$r = \sqrt{\langle \mathbf{r}, \mathbf{r} \rangle}, \qquad s = \sqrt{\langle \mathbf{s}, \mathbf{s} \rangle}, \qquad \phi = \cos^{-1}(\langle \mathbf{r}, \mathbf{s} \rangle / rs),$$

where $\langle \cdot, \cdot \rangle$ is the usual dot product on $\mathbf{R}^3$, and introducing coordinates

$$w_1 = r^2 - s^2, \qquad w_2 = 2rs \cos \phi, \qquad w_3 = 2rs \sin \phi > 0$$

one sees that $M \cong \mathbf{R}_+^3 = \{(w_1, w_2, w_3) : w_3 > 0\}$. As pointed out in [11], P is a trivial bundle as M is contractible to a single point. So, topologically, $P \cong \mathbf{R}_+^3 \times SO(3)$.

2.2. Nontrivial holonomy

Turning back to the action of $SO(3)$ on P, one can see that the *fundamental vector field* $\widetilde{A}$ associated with an element A in the Lie algebra $so(3)$ is given by

$$\widetilde{A}\big|_x = \frac{\mathrm{d}}{\mathrm{d}t}\bigg|_{t=0} (\mathrm{e}^{tA} x), \tag{1}$$

or equivalently,

$$\widetilde{A}\big|_x = (A\mathbf{r}, A\mathbf{s}) = (\mathbf{w} \times \mathbf{r}, \mathbf{w} \times \mathbf{s}), \tag{2}$$

where $\mathbf{w} \in \mathbf{R}^3$ is the unique vector corresponding to A by the isomorphism

$$R^{-1} : so(3) \to \mathbf{R}^3, \qquad \begin{pmatrix} 0 & -a_3 & a_2 \\ a_3 & 0 & -a_1 \\ -a_2 & a_1 & 0 \end{pmatrix} \mapsto \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}. \tag{3}$$

Let N be an orbit of the $SO(3)$ action, say $N = SO(3)x$ for a point $x \in P$; then, $T_x N = \{\widetilde{A}\big|_x : A \in so(3)\}$. Consider the orthogonal complement H_x of $T_x N$ in $T_x P$ with respect to the Euclidean dot product on P given by

$$\mathrm{d}x^2 = \langle \mathrm{d}\mathbf{r}, \mathrm{d}\mathbf{r} \rangle + \langle \mathrm{d}\mathbf{s}, \mathrm{d}\mathbf{s} \rangle. \tag{4}$$

Clearly the distribution $x \mapsto H_x$, which we call the *horizontal distribution*, defines a connection [11] $\omega : TP \to so(3)$ on P which is a special case of the *mechanical connection* defined in [19]. A vector field X^* with $X^*\big|_x \in H_x$ for all $x \in P$ is called *horizontal*. The *horizontal lift* of a vector field X on M is accordingly the unique horizontal vector field X^* on P such that $\mathrm{d}\pi(X^*) = X$. We have $\omega(X^*) = 0$ for every horizontal vector field X^* and $\omega(\widetilde{A}) = A$ for every fundamental vector field $\widetilde{A}$. In order to compute the horizontal lifts of the coordinate vector fields $\partial_r, \partial_s, \partial_\phi$ on M, we give an explicit expression for the metric $\mathrm{d}x^2$ in (4). To this end we follow [10, 13] and introduce a frame $\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3$ in $\mathbf{R}^3$ according to

$$\mathbf{r} = r\mathbf{u}_1,$$
$$\mathbf{s} = s \cos \phi \mathbf{u}_1 + s \sin \phi \mathbf{u}_2,$$
$$\mathbf{u}_3 = \mathbf{u}_1 \times \mathbf{u}_2.$$

If Euler angles (α, β, γ) on $SO(3)$ are chosen via

$$g = \mathrm{e}^{R(\alpha \mathbf{e}_3)} \mathrm{e}^{R(\beta \mathbf{e}_2)} \mathrm{e}^{R(\gamma \mathbf{e}_3)}, \qquad 0 \leqslant \alpha, \gamma \leqslant 2\pi, \qquad 0 \leqslant \beta \leqslant \pi,$$

where $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ is the standard basis of $\mathbf{R}^3$, R is defined in (3) and $g\mathbf{e}_i = \mathbf{u}_i$, $i = 1, 2, 3$, then with

$$\Theta_1 = \sin \gamma \, \mathrm{d}\beta - \sin \beta \cos \gamma \, \mathrm{d}\alpha,$$
$$\Theta_2 = \cos \gamma \, \mathrm{d}\beta + \sin \beta \sin \gamma \, \mathrm{d}\alpha,$$
$$\Theta_3 = \cos \beta \, \mathrm{d}\alpha + \mathrm{d}\gamma,$$

one obtains [13]

$$\mathrm{d}\mathbf{r} = \mathrm{d}r\mathbf{u}_1 + r\Theta_3\mathbf{u}_2 - r\Theta_2\mathbf{u}_3,$$
$$\mathrm{d}\mathbf{s} = \eta_1\mathbf{u}_1 + \eta_2\mathbf{u}_2 + \eta_3\mathbf{u}_3,$$

where

$$\eta_1 = \mathrm{d}s \cos\phi - s \sin\phi\,\mathrm{d}\phi - s \sin\phi\Theta_3,$$
$$\eta_2 = \mathrm{d}s \sin\phi + s \cos\phi\,\mathrm{d}\phi + s \cos\phi\Theta_3,$$
$$\eta_3 = s \sin\phi\Theta_1 - s \cos\phi\Theta_2.$$

In local coordinates, the metric $\mathrm{d}x^2$ then assumes the form

$$\mathrm{d}x^2 = \mathrm{d}r^2 + r^2\big(\Theta_2^2 + \Theta_3^2\big) + \eta_1^2 + \eta_2^2 + \eta_3^2.$$

This expression can be used to locally compute the horizontal lift X^* of a vector field X on M: X^* is orthogonal to $\partial_\alpha, \partial_\beta, \partial_\gamma$, and $\mathrm{d}\pi(X^*) = X$. It follows that

$$\partial_r^* = \partial_r, \qquad \partial_s^* = \partial_s, \qquad \partial_\phi^* = \partial_\phi - \frac{s^2}{r^2+s^2}\partial_\gamma. \tag{5}$$

In gauge theory, the factor $\frac{s^2}{r^2+s^2}$ is referred to as a component of a *Yang–Mills potential* [5].

2.3. Holonomy reduction

By equation (5) we have arrived at the well-known phenomenon of inseparability of rotations and vibrations [3, 6]. Namely from (5) we see that

$$[\partial_r^*, \partial_s^*] = 0, \qquad [\partial_r^*, \partial_\phi^*] = -\partial_r\left(\frac{s^2}{r^2+s^2}\right)\partial_\gamma, \qquad [\partial_s^*, \partial_\phi^*] = -\partial_s\left(\frac{s^2}{r^2+s^2}\right)\partial_\gamma.$$

Thus, the distribution spanned by $\partial_r^*, \partial_s^*, \partial_\phi^*$ is not integrable, and hence, if these vector fields are considered as infinitesimal vibrational motions, one can say that vibrations generate rotations. This is why the internal space M is not a submanifold of P [5]. On the other hand, $\partial_r^*, \partial_s^*, \partial_\phi^*, \partial_\gamma$ do span an involutive and hence integrable distribution. The maximal integral manifold Q_x of that distribution at a point $x \in P$ is a good candidate for being the reduced configuration space because vibrational motions through x live in that space. In fact, we will obtain the reduced dynamics of a triatomic molecule on the cotangent bundle over Q_x by employing the holonomy reduction of principal bundles. A curve on P is called horizontal if its tangents are horizontal. Fix a point $x \in P$ and denote by $P(x)$ the set of all points in P which can be joined to x by horizontal curves. It is known that [3, 10] the holonomy group of ω is $SO(2)$ (see also appendix A), and since M is connected and paracompact, the holonomy reduction theorem [17] implies that $P(x)$ is a reduced bundle with the structure group $SO(2)$, which is in fact Q_x. Furthermore, Q_x is a trivial bundle as it has the same base space as P. Since the holonomy bundles for different x are isomorphic it is common to drop the reference to the base point x [17]. We will therefore from now on write Q instead of Q_x, which also explains the notation we already used in the introduction. The observations above suggest that the reduced configuration space of a triatomic molecular system is topologically $\mathbf{R}_+^3 \times SO(2)$. The induced metric on Q is thus

$$\mathrm{d}q^2 = \mathrm{d}r^2 + \mathrm{d}s^2 + \frac{r^2 s^2}{r^2+s^2}\,\mathrm{d}\phi^2 + \frac{1}{r^2+s^2}\zeta^2, \tag{6}$$

where

$$\zeta = s^2\,\mathrm{d}\phi + (r^2+s^2)\,\mathrm{d}\gamma. \tag{7}$$

Note here that reducing the configuration space to Q cannot be interpreted as reducing the problem to the planar three-body problem. The points in Q for a given base point x represent configurations of the full space P which can be joined to x by horizontal motions. The horizontal motions are in fact planar (see appendix A). However, Q should not be

5

confused with the configuration space of the planar three-body problem. By the holonomy reduction theorem, Q is a principal bundle whose base space is the internal space M. Since M is contractible the bundle Q is trivial. In contrast, the translation-reduced space in the planar three-body problem is not a trivial bundle [20]. In fact the bundle Q defined in this paper can be viewed as a subbundle of the fibre bundle that one finds in the case of the planar three-body reduction corresponding to non-collinear configurations of a given parity [10].

3. Reduced dynamics

3.1. Angular momentum

In the following, we want to put our derivation above into the context of some well-known results. It is known [1] that in the case of small vibrations one can separate vibrations and rotations in the vicinity of an equilibrium point. In the present situation, if one chooses $d\gamma = 0$ in (6) the well-known Eckart kinetic energy is obtained. This is the gauge-dependent internal metric $h_{\mu\nu}$ in [10]. Thus, one can conclude that in the case of small vibrations, the internal motions of a molecule live in the integral manifolds of the distribution spanned by $\partial_r, \partial_s, \partial_\phi$, called the *Eckart space*. Next, consider the angular momentum

$$\mathbf{J} = \mathbf{r} \times d\mathbf{r} + \mathbf{s} \times d\mathbf{s}$$

on P which is computed locally to be

$$\mathbf{J} = s \sin\phi \eta_3 \mathbf{u}_1 + (r^2\Theta_2 - s\cos\phi\eta_3)\mathbf{u}_2 + (r^2\Theta_3 + s\cos\phi\eta_2 - s\sin\phi\eta_1)\mathbf{u}_3.$$

So, its restriction to Q is

$$\mathbf{J}|_Q = \zeta\mathbf{u}_3.$$

If the angular momentum of the system is identically zero, then $\zeta = 0$, and hence

$$dq^2|_{\mathbf{J}=0} = dr^2 + ds^2 + \frac{r^2 s^2}{r^2 + s^2} d\phi^2.$$

3.2. Holonomy-reduced Hamiltonian

In the case of vanishing angular momentum the Hamiltonian is obtained to be

$$H = \frac{1}{2}p_r^2 + \frac{1}{2}p_s^2 + \frac{1}{2}\left(\frac{1}{r^2} + \frac{1}{s^2}\right)p_\phi^2 + V(r, s, \phi), \tag{8}$$

where p_r, p_s, p_ϕ are the conjugate momenta and $V(r, s, \phi)$ is the potential energy which is assumed to be rotationally invariant. This Hamiltonian is widely used in applications. By (7), we observe that vibrational motions live in the integral manifold of the distribution spanned by $\partial_r^*, \partial_s^*, \partial_\gamma$. That space may be called *zero-angular momentum space*.

If the reduced angular momentum $\mathbf{J}|_Q$ is a non-zero constant, we have $\zeta = \text{const} \neq 0$. Then, equivalently, ∂_ϕ^* is a non-zero constant and hence the vibrational motions remain in a three-dimensional affine space which is parallel to the zero-angular momentum space.

Taking into account the contribution of ζ in the induced metric dq^2 on Q in (6) the Hamiltonian in (8) changes to the general *holonomy-reduced Hamiltonian*

$$H = \frac{1}{2}p_r^2 + \frac{1}{2}p_s^2 + \frac{1}{2}\left(\frac{1}{r^2} + \frac{1}{s^2}\right)p_\phi^2 - \frac{1}{r^2}p_\phi p_\gamma + \frac{1}{2r^2}p_\gamma^2 + V(r, s, \phi).$$

The corresponding Hamiltonian vector field is given by

$$
X = p_r \partial_r + p_s \partial_s + \left(\left(\frac{1}{r^2} + \frac{1}{s^2} \right) p_\phi - \frac{1}{r^2} p_\gamma \right) \partial_\phi + \frac{1}{r^2} (p_\gamma - p_\phi) \partial_\gamma
$$
$$
+ \left(\frac{1}{r^3} (p_\gamma - p_\phi)^2 - \frac{\partial V}{\partial r} \right) \partial_{p_r} + \left(\frac{1}{s^3} p_\phi^2 - \frac{\partial V}{\partial s} \right) \partial_{p_s} - \frac{\partial V}{\partial \phi} \partial_{p_\phi}.
$$

Since γ is cyclic the conjugate momentum p_γ is conserved. To put it another way, $\mathbf{J}|_Q$ is an S^1-equivariant momentum and the standard symplectic reduction theorem can be applied. Using a theorem by Arnold (see [18], p 378), the resulting reduced phase space is again a natural mechanical system, i.e. a cotangent bundle.

4. Comments on related work

4.1. The relation between the motions of a triatomic molecule and a charged particle in a magnetic field

In [21, 22], the idea is introduced to describe the motion of a charged particle in a magnetic field by extending the configuration space $\mathbf{R}^3$ to $\mathbf{R}^3 \times S^1$ such that the angle corresponding to S^1 is cyclic and its conserved conjugate momentum gives the charge of the particle in the magnetic field. Since the holonomy-reduced configuration space is $\mathbf{R}_+^3 \times S^1$, we can identify the motion of a triatomic molecule to that of a charged particle in a magnetic field as follows. Let $\mathbf{q}$ denote a point in M with coordinates (r, s, ϕ). If A denotes the one-form $(r^2 + s^2)^{-1} \zeta = \frac{s^2}{r^2+s^2} \, \mathrm{d}\phi$ on $\mathbf{R}_+^3$, then by metric (6) the kinetic energy can be written as

$$
L_K = \frac{1}{2} \| \dot{\mathbf{q}} \|^2 + \frac{r^2 + s^2}{2} (A(\dot{\mathbf{q}}) + \dot{\gamma})^2,
$$

which is reminiscent of the so-called *Kaluza–Klein Lagrangian* [22]. The one-form A plays the role of a vector potential for the magnetic field. The conserved momentum

$$
p_\gamma = \frac{\partial L_K}{\partial \dot{\gamma}} = (r^2 + s^2)(A(\dot{\mathbf{q}}) + \dot{\gamma})
$$

is the charge $e = cp_\gamma$ (with c denoting the speed of light) [22].

4.2. Relation to symplectic and dimensional reduction

In [6], the symplectic reduction procedure [7, 8] is applied to the N-body problem. The cotangent bundle over the translation-reduced configuration space P is a symplectic manifold with the canonical two-form, and the angular momentum $J : T^*P \to so(3)$ is an equivariant momentum map. For a $\mu \neq 0$, it is shown that $J^{-1}(\mu)$ is a principal bundle with the structure group $SO(2)$ whereas the zero momentum space $J^{-1}(0)$ is a principal bundle with the structure group $SO(3)$. Furthermore $J^{-1}(0)/SO(3)$ is shown to be diffeomorphic to $T^*(P/SO(3))$, but $J^{-1}(\mu)/SO(2)$ is no more a cotangent bundle because of dimensionality. As pointed out in [6], the procedure for the latter when applied to three bodies is in fact the *elimination of nodes*.

In contrast to the symplectic reduction procedure, the first step in this paper was to pass from the translation-reduced configuration space P of a triatomic molecule to a subbundle Q (the holonomy-reduced bundle) which is a principal bundle with the structure group $SO(2)$. Afterwards, the angular momentum is then restricted to T^*Q, and finally the symplectic reduction procedure is applied. The reduced space is then always a cotangent bundle as follows from a theorem by Arnold (see [18], p 378).

We note that the method used in this work is strongly related to dimensional reduction [23, 24], a method developed for symmetries of gauge fields. An example of this is the case of spherical symmetry in six dimensions applied to an SU(3) gauge theory, where the two extra dimensions describe a sphere of radius R. One solution, with the largest set of Higgs fields, reduces to the four-dimensional Weinberg–Salam model without fermions [23].

5. Conclusions

In this paper, we used the geometric theory of molecular mechanics [3, 10, 11] to reduce the number of degrees of freedom in the molecular three-body problem. We followed the principal bundle setting of Guichardet [3] on the translation-reduced configuration space, and using the holonomy reduction theorem [17], it was possible to reduce to a principal subbundle. This may be interpreted as separating two rotational degrees of freedom from the maximal space that includes vibrational motions. It was then possible to induce the angular momentum and apply the very symplectic reduction procedure (to be precise, we used it in the form of Noether's theorem here) to reduce to a six-dimensional phase space which is a cotangent bundle, i.e. the system reduced this way is a natural mechanical system. For the case of zero angular momentum, this is the well-known separability of vibrations and rotations. In this paper, we showed that a similar separation can also be obtained for non-zero angular momentum if one chooses a holonomy-reduced configuration space. We moreover used this approach to reduction to rephrase the well-known fact [21] that a triatomic molecular system behaves like a single particle in a magnetic field.

Acknowledgment

Appendix A. A lemma by Guichardet

For completeness, we give a brief proof of the fact that a vibrational motion of a triatomic molecule, which is defined as a curve with horizontal tangents, remains in a fixed plane as originally formulated by Guichardet [3]. Let $x(t) = (\mathbf{r}(t), \mathbf{s}(t))$ be a horizontal curve on P. We show that $F_{x(t)} := \text{span}\{\mathbf{r}(t), \mathbf{s}(t)\}$ is fixed. Indeed, since $x(t)$ is horizontal it is orthogonal to all fundamental vector fields which are given in (2), and hence $\mathbf{r}(t) \times \dot{\mathbf{r}}(t) + \mathbf{s}(t) \times \dot{\mathbf{s}}(t) = 0$. That is, the angular momentum is vanishing along the curve. Let $\mathbf{y}(t)$ be a curve in $\mathbf{R}^3$ with $\langle \mathbf{y}(t), \mathbf{y}(t) \rangle = 1$ which is orthogonal to $F_{x(t)}$. By the vanishing angular momentum condition, we have $\mathbf{y}(t) \times (\mathbf{r}(t) \times \dot{\mathbf{r}}(t)) + \mathbf{y}(t) \times (\mathbf{s}(t) \times \dot{\mathbf{s}}(t)) = 0$. But this means $\langle \mathbf{y}(t), \dot{\mathbf{r}}(t) \rangle \mathbf{r}(t) + \langle \mathbf{y}(t), \dot{\mathbf{s}}(t) \rangle \mathbf{s}(t) = 0$. Then $\langle \mathbf{y}(t), \dot{\mathbf{r}}(t) \rangle = \langle \mathbf{y}(t), \dot{\mathbf{s}}(t) \rangle = 0$ follows since $\mathbf{r}(t)$ and $\mathbf{s}(t)$ are linearly independent. As $\langle \mathbf{y}(t), \dot{\mathbf{y}}(t) \rangle = 0$, $\dot{\mathbf{y}}(t)$ is in $F_{x(t)}$. And by $\langle \mathbf{y}(t), \mathbf{r}(t) \rangle = \langle \mathbf{y}(t), \mathbf{s}(t) \rangle = 0$, we have $\langle \dot{\mathbf{y}}(t), \mathbf{r}(t) \rangle = \langle \dot{\mathbf{y}}(t), \mathbf{s}(t) \rangle = 0$, which implies that $\dot{\mathbf{y}}(t)$ is orthogonal to $F_{x(t)}$. In conclusion $\dot{\mathbf{y}}(t)$ is null.

As a conclusion of the above fact, it is observed [10] that during vibrational motions or shape deformations the Jacobi vectors remain in a fixed plane, and hence the Jacobi vectors before and after the vibrational motion can be transformed to one another by a plane rotation, i.e. the holonomy group is $SO(2)$.

Appendix B. The kinematic group

Different clusterings of position vectors give rise to different choices of mass-weighted Jacobi vectors. These different choices are related to each other by transformations which are called *democracy transformations* [10]. The set of all democracy transformations forms a subgroup of the symmetry group $SO(3)$ called the *democracy* or *kinematic group*. For the three-body problem the kinematic group is $SO(2)$. This is another special feature of the three-body problem. For a recent discussion of the democracy transformations, we refer to [25].

References

[1] Eckart C 1934 Some studies concerning rotating axes and polyatomic molecules *Phys. Rev.* **47** 552–8
[2] Wilson E B, Decius J C and Cross P C 1955 *Molecular Vibrations* (New York: McGraw-Hill)
[3] Guichardet A 1984 On rotation and vibration motions of molecules *Ann. Inst. Henri Poincaré* A **40** 329–42
[4] Iwai T and Tachibana A 1986 Complete molecular Hamiltonian based on the Born–Oppenheimer adiabatic approximation *Phys. Rev.* A **33** 2262–9
[5] Iwai T and Tachibana A 1999 The geometry and mechanics of multi-particle systems *Ann. Inst. Henri Poincaré* A **70** 525–59
[6] Iwai T 1987 A geometric setting for classical molecular dynamics *Ann. Inst. Henri Poincaré* A **47** 199–219
[7] Marsden J E and Weinstein A 1974 Reduction of symplectic manifolds with symmetry *Rep. Math. Phys.* **5** 121–30
[8] Meyer K 1973 Symmetries and integrals in mechanics *Dynamical Systems* ed M Peixoto (New York: Academic) pp 259–72
[9] Shapere A and Wilczek F 1987 Self-propulsion at low Reynolds number *Phys. Rev. Lett.* **58** 2051–4
[10] Littlejohn R G and Reinsch M 1997 Gauge fields in the separation of rotations and internal motions in the N-body problem *Rev. Mod. Phys.* **69** 213–76
[11] Iwai T 1987 A geometric setting for internal motions of the quantum three body system *J. Math. Phys.* **28** 1315–26
[12] Iwai T and Yamaoka H 2005 Stratified dynamical systems and their boundary behaviour for three bodies in space, with insight into small vibrations *J. Phys. A: Math. Gen.* **38** 5709–30
[13] Iwai T and Yamaoka H 2008 Rotational-vibrational energy spectra of triatomic molecules near relative equilibria *J. Math. Phys.* **49** 043505
[14] Yanao T, Koon W S and Marsden J E 2006 Mass effects and internal space geometry in triatomic reaction dynamics *Phys. Rev.* A **73** 052704
[15] Montgomery R 1996 The geometric phase of the three-body problem *Nonlinearity* **9** 1341–60
[16] Littlejohn R G, Mitchell K A, Aquilanti V and Cavalli S 1998 Body frames and frame singularities for three-atom systems *Phys. Rev.* A **58** 3705
[17] Kobayashi S and Nomizu K 1963 *Foundations of Differential Geometry* vol 1 (New York: Interscience)
[18] Arnold V I 1978 *Mathematical Methods of Classical Mechanics* (New York: Springer)
[19] Marsden J E 1992 *Lectures on Mechanics* (Cambridge: Cambridge University Press)
[20] Iwai T 1987 A gauge theory for the quantum planar three-body problem *J. Math. Phys.* **28** 964–74
[21] Montgomery R 1990 The isoholonomic problem and some of its applications *Commun. Math. Phys.* **128** 565–92
[22] Marsden J E and Ratiu T S 1999 *Introduction to Mechanics and Symmetry* (New York: Springer)
[23] Forgács P and Manton N S 1980 Space-time symmetries in gauge theories *Commun. Math. Phys.* **72** 15–35
[24] Shnider S and Sternberg S 1983 Dimensional reduction and symplectic reduction *Nuovo Cimento* B **3** 130–9
[25] Yanao T and Takatsuka K 2003 Collective coordinates and an accompanying metric force in structural isomerization dynamics of molecules *Phys. Rev.* A **68** 032714