

Gauge Theory of Small Vibrations in Polyatomic Molecules

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Abstract

The problem of small vibrations in polyatomic molecules is examined from the standpoint of gauge theory and fiber bundle theory. The Eckart conventions and their privileged status are given a geometrical interpretation (the Eckart coordinates are shown to be Riemann normal coordinates and the Eckart frame is a non-Abelian version of Poincaré gauge). The Hamiltonian is developed in covariant Taylor series and averaged over rapid vibrations to second order. The averaged Hamiltonian is expressed in terms of geometrical objects such as the Riemann and Coriolis curvature tensors on shape space.

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1 Introduction

It is truly a pleasure to dedicate this article to Jerry Marsden, who has not only been the inspiration for much of our own work, but who has also been a good friend. We are especially grateful for the series of lectures which Jerry gave to one of us (R.L.) and his students perhaps eight or nine years ago on applications of geometrical methods to molecular dynamics. The field of geometry, symmetry and dynamics would be greatly impoverished without Jerry, and we hope he will continue to have as much influence on it (and us) in the future as he has had in the past.

The problem of small vibrations in rotating systems is an intrinsically interesting one. Here we find corrections to rigid body behavior for a body which is “stiff” but not infinitely so, so that it is capable of small amplitude, high frequency vibrations as it undergoes slower rotations. Since a rigid body is an idealization which does not exist in nature, we can see in this problem how the idealization comes about as the limit of a more realistic system.

One of the most physically important and well studied examples of a nearly rigid body is a molecule, with important fundamental work going back to the 1930’s. The current status of this field and references to the earlier literature are presented in standard books on molecular physics (for example, Wilson, Decius and Cross [1955], Papoušek and Aliev [1982] and Zare [1988]). The standard approach to small vibrations is to expand the Wilson-Howard-Watson Hamiltonian (Watson [1968]) about an equilibrium position. This Hamiltonian is committed to the Eckart conventions (Eckart [1935], Wilson, Decius and Cross [1955], Louck and Galbraith [1976], Biedenharn and Louck [1981] and Ezra [1982]), which consist of a privileged choice of body frame (or gauge) as a field over shape space, and a privileged choice of coordinates on shape space. The form of this Hamiltonian and the operations performed on it in the standard analysis of small vibrations are intricately entwined with the Eckart conventions, so that it is very difficult to see what the geometrical meaning is of the various terms and expressions which result. It is generally believed in the molecular literature that the Eckart conventions have overwhelming advantages for problems involving small amplitude motions, although we have found it difficult to find a completely clear examination of the issue. One of the results of this article is to confirm many of these assumptions and to place them within the geometrical framework of fiber bundle theory.

The traditional molecular literature is fundamentally coordinate-based and non-geometrical in nature. This situation began to change in the 1980’s, with the realization (by Guichardet [1984], Iwai [1986], Tachibana and Iwai [1986] and Shapere and Wilczek [1989]) that the separation of rotations from internal motions involves a certain non-Abelian, $SO(3)$ gauge field (the Coriolis field), and that the proper geometrical framework for understanding this problem is that of fiber bundle theory. The situation is reviewed by Littlejohn and Reinsch [1997], who integrate the newer approaches with the traditional literature. These newer developments have been expressed in terms of the geometry of configuration space, rather than phase space, and so have been somewhat independent of the earlier and more general theory of reduction (Abraham and Marsden [1978], Marsden and Ratiu [1994]). But of course we are dealing here with a special case of reduction theory, in which the symmetry group acts primarily on configuration space (probably the most important case from a physical standpoint).

The purpose of this article is to examine small vibrations of a molecule from a completely covariant and gauge-invariant standpoint. One of our results is to show that the Eckart

frame and coordinates do have a privileged status in the analysis of small vibrations, and to explain the geometrical significance of this fact. As we will show, the Eckart coordinates turn out to be identical with Riemann normal coordinates on shape space and the Eckart frame is a non-Abelian version of Poincaré gauge.

One of the main results of a theory of small vibrations is the form of the Hamiltonian averaged over the rapid vibrations (the normal form), our Eqs. (4.9) and (4.10). This Hamiltonian contains information about shifts in energy levels due to the “Coriolis coupling,” the “centrifugal distortion” and other physical effects. Since energy level shifts are physically observable, they cannot depend on conventions for body frame (gauge) or coordinate system, Eckart or otherwise. Therefore we believed when we started this work that these physical effects must be expressible in manifestly gauge-invariant and coordinate-invariant form, presumably involving the Coriolis curvature tensor $\mathbf{B}_{\mu\nu}$ (rather than the gauge potential \mathbf{A}_μ), the Riemann curvature tensor $R^\mu{}_{\nu\alpha\beta}$ etc. Indeed this is precisely what we found. Nevertheless, the Eckart conventions are involved in deriving these results, as we will show.

We proceed by analyzing small vibrations in diatomic molecules, then we set up the reduced Hamiltonian for polyatomic molecules and discuss choices of gauges which simplify the perturbation analysis. A model problem involving small vibrations in a $U(1)$ (electromagnetic) gauge field leads us to the choice of Poincaré gauge, and similarly we are led to choose Riemann normal coordinates to simplify the expansion of the Hamiltonian. These are shown to be identical to Eckart’s conventions. We next develop the Hamiltonian in a covariant Taylor series expansion, and then average it (transform it to normal form). The results are briefly discussed. Finally we present some conclusions and ideas for new applications.

2 The Perturbation Problem

2.1 Small Vibrations in One Dimension

The small vibrations of a particle of mass m moving near the bottom of a one-dimensional potential $V(x)$ is described by the Hamiltonian,

$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} + \kappa V_3 \frac{x^3}{6} + \kappa^2 V_4 \frac{x^4}{24} + \dots, \quad (2.1)$$

where we have expanded the potential about the minimum at $x = 0$, denoted the n -th derivative of the potential at $x = 0$ by V_n , introduced the frequency of small vibrations ω by writing $V_2 = m\omega^2$, dropped the constant term $V(0)$, and introduced a formal ordering parameter κ which indicates the order of the successive terms. Equation (2.1) is the starting point for the transformation to Birkhoff normal form (Birkhoff [1927], Eckhardt [1986]), which we carry out in action-angle variables (θ, I) ,

$$x = \left(\frac{2I}{m\omega} \right)^{1/2} \sin \theta, \quad p = (2Im\omega)^{1/2} \cos \theta. \quad (2.2)$$

The sequence of canonical transformations which formally eliminates the angle dependence of the Hamiltonian is conveniently carried out using Lie transform methods (Cary [1981],

Dragt and Finn [1976]), which through terms quadratic in the action yield the averaged Hamiltonian,

$$K = I\omega + \kappa^2(I\omega)^2 \left(-\frac{5V_3^2}{48m^3\omega^6} + \frac{V_4}{16m^2\omega^4} \right) + \dots \quad (2.3)$$

The first correction in K occurs at second order in κ , since all terms first order in κ average to zero; this correction contains the nonlinear frequency shift, a physically important quantity.

2.2 Small Vibrations of a Diatomic Molecule

Consider now the small vibrations of a diatomic molecule, from the classical standpoint (see, example, Wilson, Decius and Cross [1955], Kroto [1975], or Bunker [1979]). The Hamiltonian for the radial coordinate (the reduced Hamiltonian for the two-body problem) is

$$H = \frac{p^2}{2m} + \frac{L^2}{2mr^2} + V(r), \quad (2.4)$$

where p is the momentum conjugate to r , m is the reduced mass of the two atoms (of the order of an atomic mass), L is the magnitude of the angular momentum (a constant), and $V(r)$ is the Born-Oppenheimer potential, assumed to have a minimum at $r = r_0$. We do not simply expand the total potential (true plus centrifugal) about its minimum, because there are slightly nontrivial ordering issues.

To expand and order this Hamiltonian in a physically realistic manner, we must specify physically interesting values of the parameters and initial conditions. These depend on the physical circumstances, so the ordering scheme is not unique, but the following is a common and reasonable approach. We begin with atomic units, in which m_e (the electron mass), \hbar (Planck's constant) and e (the electron charge) are all set to unity. Then a typical nuclear (or atomic) mass is of the order of 10^4 , which we regard as order κ^{-4} (this is standard Born-Oppenheimer ordering). The potential $V(r)$ is independent of the nuclear mass and so is regarded as of order $\kappa^0 = 1$. This applies not only to the depth $V(r_0)$ of the potential but also to its approximate range r_0 , its spring constant $k = V_2 = V''(r_0)$, etc. However, the frequency $\omega = (k/m)^{1/2}$ of small vibrations involves the nuclear mass, and thus turns out to be of order κ^2 . Thus these vibrations are slower than typical electronic motions by a factor of κ^{-2} (that is, about 100).

Next we assume the initial conditions are consistent with a vibrational quantum number of order unity (that is, independent of κ). This is a reasonable assumption at ordinary temperatures. Thus the vibrational amplitude $x = r - r_0$ (the displacement from equilibrium) is of order $(\hbar/m\omega)^{1/2}$, that is, of order κ . This in turn implies that the vibrational energy is of order κ^2 , the vibrational velocity $v = \dot{x}$ is of order κ^3 , and the vibrational momentum $p = mv$ is of order κ^{-1} . Finally there is the question of the order of magnitude of the angular momentum L , which also depends on the initial conditions. We will assume, in accordance with thermal equilibrium, that the vibrational energy and the rotational kinetic energy, $L^2/2mr^2$, are comparable, that is, of order κ^2 . This implies that L , or, equivalently, the angular momentum quantum number ℓ , is of order κ^{-1} . Note that with this ordering, the moment of inertia M is of order κ^{-4} , and hence the rotational frequency $\Omega_r = M^{-1}L$ is of order κ^3 . This is a factor of κ times slower than the vibrational frequency, so we have an adiabatic separations of time scales between the vibrational and rotational motions. The molecule vibrates on the order of 10 times during each rotation.

Other ordering schemes than the one we have presented are possible, but correspond to different physical circumstances. Our assumptions regarding the rotational kinetic energy imply that the amount of centrifugal distortion is small, namely, of order κ . Thus, the shape of the molecule at a minimum of the potential energy is nearly the same as the shape in a relative (rotating) equilibrium, and the difference between the two can be handled by perturbation theory. This may be a disappointment to those interested in the theory of relative equilibria, which is an important part of the rest of this volume. The situation would be different for rapidly rotating molecules; in this case, studies have been carried out by Jellinek and Li [1989], Kozin, Roberts and Tennyson [2000] and others. However, such rapid rotation is unusual from a physical standpoint, and is of less common interest than the case we consider here. The ordering scheme we have developed is equivalent to that developed by Nielson (discussed in Papoušek and Aliev [1982]).

Although we have used quantum concepts to work out the ordering of various quantities, we will carry out a classical treatment of the Hamiltonian. This is reasonable since the classical treatment closely parallels the proper quantum treatment, and in any case is good practice before doing the quantum calculation.

To introduce a formal ordering parameter consistent with the Nielson ordering scheme, we make the substitutions $m = m'/\kappa^4$, $r = r_0 + \kappa x'$, $p = p'/\kappa$ and $L = L'/\kappa$ in the Hamiltonian (2.4). We note that $(r, p) \rightarrow (x', p')$ is a canonical transformation. Then we drop the primes, expand both the true potential $V(r_0 + \kappa x)$ and the centrifugal potential $L^2/2m(r_0 + \kappa x)^2$ in κ , and drop the constant $V(r_0)$. Finally, we cancel an overall factor of κ^2 from the Hamiltonian, or, equivalently, set $t = t'/\kappa^2$, which means working with a new time variable in which the vibrational time scale is of order unity. The result is the Hamiltonian $H = \sum_{n=0}^{\infty} \kappa^n H_n$, where

$$H_0 = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} + \frac{L^2}{2mr_0^2}, \quad (2.5)$$

$$H_n = (-1)^n (n+1) \frac{L^2}{2mr_0^2} \left(\frac{x}{r_0}\right)^n + \frac{V_{n+2}}{(n+2)!} x^{n+2}, \quad n > 0. \quad (2.6)$$

The third term in Eq. (2.5) is the rotational kinetic energy at lowest order; it is a constant, but we retain it in the Hamiltonian because it depends on L , and we often wish to know how the energy depends on L . Otherwise it has no effect on the following analysis. The first term in Eq. (2.6) can be thought of as representing the effects of centrifugal distortion. This is particularly clear in the case $n = 1$, where this term is proportional to x and can be incorporated into the harmonic oscillator in H_0 by completing the square, that is, by shifting the origin. The new origin is approximately the equilibrium configuration in the rotating system. Indeed, it would be possible to expand the total potential (true plus centrifugal) about the minimum of the total potential, rather than that of the true potential only, as done here. The result would be a reorganization of the expansion, with some first order terms being absorbed into zeroth order terms. This does not, however, seem to offer any great advantages.

We now transform this Hamiltonian to action-angle variables as before and apply the normal form or averaging transformation. Writing $\sum_n \kappa^n K_n$ for the averaged Hamiltonian,

we find $K_n = 0$ for n odd, and

$$K_0 = I\omega + \frac{L^2}{2mr_0^2}, \quad (2.7)$$

$$\begin{aligned} K_2 = & (I\omega)^2 \left(-\frac{5V_3^2}{48m^3\omega^6} + \frac{V_4}{16m^2\omega^4} \right) \\ & + (I\omega) \left(\frac{L^2}{2mr_0^2} \right) \left(\frac{3}{m\omega^2 r_0^2} + \frac{V_3}{m^2\omega^4 r_0} \right) - \left(\frac{L^2}{2mr_0^2} \right)^2 \frac{2}{m\omega^2 r_0^2}. \end{aligned} \quad (2.8)$$

Hamilton's equation $\Omega_r = \partial K / \partial L$ gives the angular velocity Ω_r of rotation of the molecule (valid for a diatomic), which for a rigid body would be $M^{-1}L$, where M is the moment of inertia. If we use this rigid body formula also in the case of the vibrating molecule, we effectively define M^{-1} for a non-rigid molecule. We then find that M^{-1} is given by its equilibrium value $1/mr_0^2$ plus one correction proportional to L^2 and another proportional to the vibrational action I . The first of these corrections indicates the centrifugal distortion, that is, the distortion to the shape of the rotating molecule due to centrifugal forces, and the second is the correction to the moment of inertia due to the vibrations, averaged over the rapid vibrations. The other one of Hamilton's equations, $\Omega_v = \partial K / \partial I$, gives the vibrational frequency Ω_v , which is ω (the frequency of small vibrations) plus a correction proportional to I (due to the nonlinearity of the potential) and another proportional to L^2 . The latter indicates the nonvanishing average of the centrifugal forces over the rapid vibrations (compared to the slower rotations).

This calculation was classical, but a good approximation to the correct quantum result is obtained by replacing L^2 by $\ell(\ell+1)\hbar^2$ and I by $(n+1/2)\hbar$, where n is the vibrational quantum number. From the observed spectrum of the molecule (differences between energy levels) it is possible to determine the parameters of the Hamiltonian (ω , r_0 , V_3 , V_4).

2.3 The Hamiltonian for Small Vibrations in Polyatomic Molecules

Let us now consider the small vibrations of a polyatomic molecule with $N \geq 3$ atoms, modelled as a system of point masses interacting via a Born-Oppenheimer potential V . The first problem is to write down the reduced Hamiltonian (that is, reduced with respect to the translational and rotational invariance of the system). This is an old subject. Here we follow the notation of Littlejohn and Reinsch [1997], which is based on local coordinate patches and local sections on the quotient (shape) space. It is understood that all constructions (coordinates, section and fields over shape space) are local, which is all we need for the problem of small vibrations. We let $\{\mathbf{r}_{s\alpha}, \alpha = 1, \dots, N\}$ be the positions of the N atoms, referred to the inertial or "space" frame (hence the s subscript). The translational degrees of freedom are eliminated by going to the center-of-mass frame, in which only $N-1$ vectors $\{\boldsymbol{\rho}_{s\alpha}, \alpha = 1, \dots, N-1\}$ are needed to specify the configuration. We choose these vectors to be mass-weighted Jacobi vectors, which means that the kinetic energy is Euclidean, that is, it has the form $(1/2) \sum_{\alpha} |\boldsymbol{\rho}_{s\alpha}|^2$. The translation-reduced configuration space is \mathbb{R}^{3N-3} , which is foliated by the action of $SO(3)$ to produce an $SO(3)$ fiber bundle plus singular orbits, the latter consisting of the collinear configurations. Generic orbits are fibers, diffeomorphic to $SO(3)$. The quotient space $\mathbb{R}^{3N-3}/SO(3)$ is "shape space," the base space of the bundle plus

the singular (collinear) shapes. We introduce a coordinate system $\{q^\mu, \mu = 1, \dots, 3N - 6\}$, essentially arbitrary at this point, on shape space. We also introduce a section of the fiber bundle, also essentially arbitrary at this point, which is equivalent to the definition of a body frame (a configuration on the section is one for which the body frame and space frame coincide). The s subscript is omitted on vectors and tensors referred to the body frame.

The Hamiltonian is expressed in terms of three fields over shape space, defined by

$$\mathbf{M} = \sum_{\alpha} \rho_{\alpha} \otimes \rho_{\alpha} - |\rho_{\alpha}|^2 \mathbf{I}, \quad (2.9)$$

$$\mathbf{A}_{\mu} = \mathbf{M}^{-1} \sum_{\alpha} \rho_{\alpha} \times \frac{\partial \rho_{\alpha}}{\partial q^{\mu}}, \quad (2.10)$$

$$g_{\mu\nu} = \sum_{\alpha} \frac{\partial \rho_{\alpha}}{\partial q^{\mu}} \cdot \frac{\partial \rho_{\alpha}}{\partial q^{\nu}} - \mathbf{A}_{\mu} \cdot \mathbf{M} \cdot \mathbf{A}_{\nu}, \quad (2.11)$$

where \mathbf{M} is the moment of inertia tensor, \mathbf{I} is the identity tensor, \mathbf{A}_{μ} is the Coriolis gauge potential, and $g_{\mu\nu}$ is the metric tensor on shape space. Then the translation- and rotation-reduced Hamiltonian is

$$H = \frac{1}{2} \mathbf{L} \cdot \mathbf{M}^{-1} \cdot \mathbf{L} + \frac{1}{2} v_{\mu} g^{\mu\nu} v_{\nu} + V(q), \quad (2.12)$$

where \mathbf{L} is the angular momentum and where v_{μ} is the covariant “shape” velocity, given in terms of the p_{μ} , the momentum conjugate to q^{μ} , by

$$v_{\mu} = p_{\mu} - \mathbf{L} \cdot \mathbf{A}_{\mu}. \quad (2.13)$$

The three terms in the Hamiltonian (2.12) are the vertical kinetic energy, the horizontal kinetic energy and the potential energy. We also need the symplectic 1-form to find equations of motion, which is $\theta = p_{\mu} dq^{\mu} + L_i \lambda_i$, where λ_i , $i = 1, 2, 3$, are the left-invariant 1-forms on $SO(3)$, transported to the rotation fibers in \mathbb{R}^{3N-3} . The absence of the s -subscript on ρ_{α} , \mathbf{M} , \mathbf{A}_{μ} and \mathbf{L} indicates the body frame. Thus, the components L_i satisfy the usual (body frame) Poisson bracket relations, $\{L_i, L_j\} = -\epsilon_{ijk} L_k$.

Now suppose q_0 is an equilibrium shape, that is, one for which $\partial V / \partial q^{\mu} = 0$. We assume that q_0 is a noncollinear shape (it lies on a generic orbit of $SO(3)$). We wish to study small vibrations about this equilibrium. We use Nielson ordering for this purpose, which as above involves writing $m_{\alpha} = m'_{\alpha} / \kappa^4$, $q^{\mu} = q_0^{\mu} + \kappa x'^{\mu}$, $p_{\mu} = p'_{\mu} / \kappa$, $\mathbf{L} = \mathbf{L}' / \kappa$ and $t = t' / \kappa^2$. This is less trivial than in the diatomic case, because now \mathbf{L} is a nontrivial dynamical variable. In addition, we set $\rho_{\alpha} = \rho'_{\alpha} / \kappa^2$ (because the Jacobi vectors are “mass-weighted,” that is, they have absorbed factors of the square root of the atomic masses to make the kinetic energy Euclidean), $\mathbf{M} = \mathbf{M}' / \kappa^4$, $\mathbf{A}_{\mu} = \mathbf{A}'_{\mu}$, $g_{\mu\nu} = g'_{\mu\nu} / \kappa^4$, $g^{\mu\nu} = g'^{\mu\nu} \kappa^4$, $v_{\mu} = v'_{\mu} / \kappa$ and $v^{\mu} = v'^{\mu} \kappa^3$, which follow from the definitions above. The gauge potential \mathbf{A}_{μ} is independent of κ because the angle of rotation of the “falling cat” is invariant when all masses are scaled by the same amount. We substitute these into the Hamiltonian, drop the primes, scale H by κ^2 (which is the effect of the scaling of time), expand the potential and drop the constant $V(q_0)$. The result is

$$H = \frac{1}{2} \mathbf{L} \cdot \mathbf{M}^{-1} \cdot \mathbf{L} + \frac{1}{2} v_{\mu} g^{\mu\nu} v_{\nu} + \frac{1}{2} V_{,\mu\nu} x^{\mu} x^{\nu} + \frac{\kappa}{6} V_{,\mu\nu\sigma} x^{\mu} x^{\nu} x^{\sigma} + \dots, \quad (2.14)$$

where $V_{,\mu\nu}$, $V_{,\mu\nu\sigma}$, etc., are the q -derivatives of the potential evaluated at equilibrium (commas represent ordinary derivatives), and where it is understood that \mathbf{M} , \mathbf{A}_μ (contained in v_μ) and $g^{\mu\nu}$ are evaluated at $q_0^\mu + \kappa x^\mu$. If these dependencies are also expanded out, H is arranged as a power series in κ (it is also quadratic in \mathbf{L} , quadratic in p_μ , and a power series in x^μ). The symplectic form also becomes ordered in κ ; it is now

$$\theta = p_\mu dx^\mu + \frac{1}{\kappa} L_i \lambda_i. \quad (2.15)$$

Symplectic forms which are ordered like this into “large” and “small” parts are a standard occurrence in problems with multiple time scales. They are easily handled in perturbation theory by using a Poisson bracket which is correspondingly ordered; in this case, we have

$$\{f, g\} = \sum_\mu \left(\frac{\partial f}{\partial x^\mu} \frac{\partial g}{\partial p_\mu} - \frac{\partial f}{\partial p_\mu} \frac{\partial g}{\partial x^\mu} \right) - \kappa \mathbf{L} \cdot \left(\frac{\partial f}{\partial \mathbf{L}} \times \frac{\partial g}{\partial \mathbf{L}} \right). \quad (2.16)$$

Examples of such perturbation problems are presented in Littlejohn [1979] (for guiding center motion) and Littlejohn and Weigert [1993] (for the Stern-Gerlach problem). In this case, the slow angular momentum Poisson bracket indicates the slow time scale of rotations, in comparison to vibrations. Corresponding problems in quantum mechanics can be handled by a kind of Weyl symbol perturbation theory, for which see Littlejohn and Flynn [1991], [1992] and Weigert and Littlejohn [1993], or in other cases by Van Vleck perturbation theory (Zare, [1988]).

The Hamiltonian (2.12) is written in an arbitrary coordinate system and gauge (it is manifestly covariant), in contrast to the usual custom in the study of small vibrations in the molecular literature, where the Hamiltonian is specialized to the Eckart conventions for gauge and shape coordinates. Moreover, it is the usual custom in the molecular literature to complete the square in the angular momentum \mathbf{L} in a different way, thereby introducing new tensor-like fields (the “modified” inverse moment of inertia tensor and others) which are not true tensor fields. The effect is to obscure the geometrical meaning of the result. Our aim will be to maintain manifest covariance throughout. One can give a geometrical interpretation to the Eckart frame (discussed in Littlejohn and Reinsch [1997]), but this by itself does not explain whether the Eckart frame really has special virtues for the analysis of small vibrations.

On the other hand, a straightforward expansion of the Hamiltonian (2.14) in a power series in κ produces quite a few terms even through second order, and it is natural to ask whether a special choice of gauge or coordinate system will simplify these or the perturbation analysis itself. The issue is already seen in the zeroth order term of Eq. (2.14),

$$H_0 = \frac{1}{2} \mathbf{L} \cdot \mathbf{M}_0 \cdot \mathbf{L} + \frac{1}{2} (p_\mu - \mathbf{L} \cdot \mathbf{A}_{0\mu}) g_0^{\mu\nu} (p_\nu - \mathbf{L} \cdot \mathbf{A}_{0\mu}) + \frac{1}{2} V_{,\mu\nu} x^\mu x^\nu, \quad (2.17)$$

where the 0-subscripts indicate that the fields are evaluated at q_0 . It is not even clear that this Hamiltonian has effected a separation of vibrational and rotational motions at lowest order, due to the presence of the terms in $\mathbf{L} \cdot \mathbf{A}_{0\mu}$. Thus one is motivated to perform a gauge transformation such that in the new gauge, \mathbf{A}_μ vanishes at the equilibrium shape. The desirability of doing this was apparently first noted by Casimir [1931]. The geometrical condition for this is that the section should be orthogonal to the equilibrium fiber where

it intersects that fiber; in fact, the Eckart section has this property, but so do many other choices of gauge, so it is still not clear that the Eckart choice is the best.

In any case, in such a gauge, the vertical kinetic energy becomes a function only of \mathbf{L} (it is the rigid body kinetic energy for the molecule in the equilibrium shape), and the rest of H_0 is a harmonic oscillator. To bring out the harmonic oscillator more clearly, we may first choose our coordinates q^μ to be orthogonal at the equilibrium shape, so that $g_0^{\mu\nu} = g_{0\mu\nu} = \delta_{\mu\nu}$. The horizontal kinetic energy is then $(1/2) \sum_\mu p_\mu^2$. Then by a further, orthogonal transformation of coordinates, we can diagonalize $V_{,\mu\nu}$. With ω_μ^2 denoting the (presumed positive) eigenvalues, the unperturbed Hamiltonian takes on the form

$$H_0 = \frac{1}{2} \mathbf{L} \cdot \mathbf{M}_0 \cdot \mathbf{L} + \frac{1}{2} \sum_\mu (p_\mu^2 + \omega_\mu^2 x_\mu^2), \quad (2.18)$$

in which it is clear that rotations and vibrations are decoupled. Higher order terms will couple these degrees of freedom, of course, and introduce shifts in the energy levels of H_0 ; that is where the real work lies. Before proceeding, however, we will examine a model problem which will help us address the question of privileged choices of gauge for simplifying the perturbation calculation.

3 Special Gauges, Frames and Coordinates

3.1 A Model Problem

In order to address issues concerning small vibrations in the presence of a gauge field, let us consider an Abelian, $U(1)$ problem before attacking the non-Abelian, $SO(3)$ problem of small vibrations in a molecule. Specifically, let us consider a 3-dimensional harmonic oscillator perturbed by a magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$. The Hamiltonian is

$$H = \frac{1}{2} (\mathbf{p} - \mathbf{A})^2 + \frac{1}{2} \sum_i \omega_i^2 x_i^2, \quad (3.1)$$

where we have set $m = 1$ and absorbed other physical constants into the vector potential \mathbf{A} . The frequencies of the harmonic oscillator in the three directions are ω_i , $i = 1, 2, 3$; these are assumed to be rationally independent, for simplicity. The magnetic field is allowed to be inhomogeneous, but the vibrational amplitude is assumed to be small compared to the scale length of the magnetic field, so field gradients are sampled only weakly. The effect of these assumptions is captured by an expansion and ordering of the vector potential,

$$\mathbf{A}(\mathbf{x}) = \mathbf{A}(0) + \kappa \mathbf{x} \cdot \nabla \mathbf{A}(0) + \frac{\kappa^2}{2} \mathbf{x} \mathbf{x} : \nabla \nabla \mathbf{A}(0) + \dots, \quad (3.2)$$

where κ is the ordering parameter.

We expect the magnetic field to have an effect on the vibrational frequencies and to give them a dependence on the actions. These effects should be gauge-invariant, that is, they should be expressible as a function of the magnetic field and its gradients alone. However, if we work in an arbitrary gauge, then even the unperturbed Hamiltonian is unattractive,

$$H_0 = \frac{1}{2} [\mathbf{p} - \mathbf{A}(0)]^2 + \frac{1}{2} \sum_i \omega_i^2 x_i^2, \quad (3.3)$$

because of the presence of the constant vector $\mathbf{A}(0)$. It is possible to do the perturbation calculation in an arbitrary gauge, but it is certainly more convenient to transform to a gauge in which $\mathbf{A}(0) = 0$. Similar transformations are suggested at each higher order, the effect of which is to express the vector potential near $\mathbf{x} = 0$ as a power series in \mathbf{x} in which the coefficients depend only on \mathbf{B} and its gradients. If these transformations are not made, the perturbation analysis can still be carried out, but since the answers do turn out to depend only on \mathbf{B} and its gradients, any terms in the expansion of \mathbf{A} which do not contribute to the final answers (for example, the symmetric part of $\nabla\mathbf{A}(0)$) drop out of the analysis. Thus, it is convenient to perform a series of gauge transformations to eliminate these superfluous terms. The details are unimportant, but what emerges is a power series representation of Poincaré gauge, given by

$$\begin{aligned}\mathbf{A}(\mathbf{x}) &= \int_0^1 t dt \mathbf{B}(t\mathbf{x}) \times \mathbf{x} \\ &= \left(\frac{1}{2}\mathbf{B}(0) + \frac{1}{3}\mathbf{x} \cdot \nabla \mathbf{B}(0) + \frac{1}{8}\mathbf{x}\mathbf{x} : \nabla\nabla\mathbf{B}(0) + \dots \right) \times \mathbf{x}.\end{aligned}\quad (3.4)$$

Poincaré gauge is defined by the integral formula on the first line (which is Poincaré's formula for uncurling a vector field); we remark that a completely equivalent definition is $\mathbf{x} \cdot \mathbf{A}(\mathbf{x}) = 0$ (the gauge is transverse in real space). Poincaré gauge is used in low-energy quantum electrodynamics (Cohen-Tannoudji [1989]), where it is useful for expressing the interaction of a localized charge and current distribution with the electromagnetic field in terms of the field and its gradients at the center of the distribution. The purpose here is similar, since the amplitude of vibration is small compared to field scale lengths.

Even in Poincaré gauge, the perturbation analysis of the Hamiltonian (3.1) is not entirely trivial. It helps to use the following formula for the second order averaged Hamiltonian, valid for an arbitrary, bound, nonresonant system of N degrees of freedom. Let $H = H_0 + \kappa H_1 + \kappa^2 H_2 + \dots$, where the action-angle variables are $(\boldsymbol{\theta}, \mathbf{I})$, where H_0 depends only on \mathbf{I} , where $\boldsymbol{\omega} = \partial H_0 / \partial \mathbf{I}$, where the other terms in H are expanded in Fourier series according to $H_k(\boldsymbol{\theta}, \mathbf{I}) = \sum_{\mathbf{n}} H_{k\mathbf{n}}(\mathbf{I}) \exp(i\mathbf{n} \cdot \boldsymbol{\theta})$ for $k \geq 1$. Vectors \mathbf{I} , $\boldsymbol{\theta}$, $\boldsymbol{\omega}$ and \mathbf{n} are N -vectors, and \mathbf{n} consists of integers. Then the first order averaged Hamiltonian is $K_1 = H_{10}$, the $\mathbf{n} = (0, \dots, 0)$ Fourier component of H_1 , and the second order averaged Hamiltonian is given by

$$K_2 = H_{20} - \frac{1}{2} \sum_{\mathbf{n} \neq 0} \mathbf{n} \cdot \frac{\partial}{\partial \mathbf{I}} \left(\frac{|H_{1\mathbf{n}}|^2}{\mathbf{n} \cdot \boldsymbol{\omega}} \right). \quad (3.5)$$

With the help of Eq. (3.5) and working in Poincaré gauge, we can carry out the perturbation analysis of small vibrations in a magnetic field through second order. The averaged Hamiltonian is given by $K = K_0 + \kappa^2 K_2$, where

$$K_0 = \sum_i \omega_i I_i, \quad (3.6)$$

$$K_2 = \frac{1}{4} \sum_{i \neq j} B_{ij}^2 \frac{\omega_i I_i - \omega_j I_j}{\omega_i^2 - \omega_j^2}, \quad (3.7)$$

where $B_{ij} = \epsilon_{ijk} B_k$, and where it is understood that the magnetic field is evaluated at $\mathbf{x} = 0$. Not surprisingly, the first nonvanishing correction only involves the strength of the

magnetic field at the origin (gradients will appear at higher order); also not surprising is the fact that the correction is linear in the actions, since a harmonic oscillator in a constant magnetic field is altogether a linear problem.

3.2 Non-Abelian Poincaré Gauge

Let us now return to the problem of small vibrations in the molecule, where the gauge field \mathbf{A}_μ is non-Abelian, and ask whether something like Poincaré gauge could be useful there. An obvious guess is that a non-Abelian version of Poincaré gauge should satisfy $x^\mu \mathbf{A}_\mu(x) = 0$, where as above x^μ is the coordinate difference from the equilibrium q_0^μ . Amazingly enough, this condition is once again equivalent to an integral formula connecting the gauge potential \mathbf{A}_μ and the Coriolis field tensor $\mathbf{B}_{\mu\nu}$, defined by

$$\mathbf{B}_{\mu\nu} = \frac{\partial \mathbf{A}_\nu}{\partial q^\mu} - \frac{\partial \mathbf{A}_\mu}{\partial q^\nu} - \mathbf{A}_\mu \times \mathbf{A}_\nu. \quad (3.8)$$

Namely, the integral formula is

$$\mathbf{A}_\mu(x) = \int_0^1 dt \, tx^\nu \mathbf{B}_{\nu\mu}(tx). \quad (3.9)$$

The result is amazing because the relation between \mathbf{A}_μ and \mathbf{B}_μ in Eq. (3.8) is nonlinear, but it is linear in Eq. (3.9). The equivalence of $x^\mu \mathbf{A}_\mu(x) = 0$ and Eq. (3.9) is known in particle physics (Halpern [1979]), but otherwise we do not know its history.

To prove these results, we use bold face symbols for 3-vectors (for example, \mathbf{A}_μ and $\mathbf{B}_{\mu\nu}$), and sans serif symbols for the corresponding 3×3 antisymmetric matrices belonging to the Lie algebra of $SO(3)$ (for example, A_μ and $B_{\mu\nu}$), where, for example, $A_{\mu ij} = \epsilon_{ijk} A_{\mu k}$. Now let $\mathbf{A}'_\mu(x)$ represent an arbitrary choice of gauge (that is, body frame). First we show that it is always possible to transform to a new gauge where $x^\mu \mathbf{A}_\mu(x) = 0$. A general gauge transformation is specified by a matrix field $\mathbf{S}(x) \in SO(3)$,

$$\mathbf{A}_\mu = \mathbf{S} \mathbf{A}'_\mu \mathbf{S}^t + \frac{\partial \mathbf{S}}{\partial x^\mu} \mathbf{S}^t. \quad (3.10)$$

Thus, if we demand that $x^\mu \mathbf{A}_\mu = 0$, we obtain a differential equation for \mathbf{S} ,

$$x^\mu \frac{\partial \mathbf{S}}{\partial x^\mu} = -x^\mu \mathbf{S} \mathbf{A}'_\mu, \quad (3.11)$$

which can always be solved (locally) by integrating along radial lines in the x^μ coordinates (we choose initial conditions $\mathbf{S}(0) = \mathbf{I}$).

The geometrical interpretation of this construction is illustrated in Fig. 5.1. In the figure, q_0 is the equilibrium shape on shape space SS , F_0 is the fiber above it, diffeomorphic to $SO(3)$, and Q_0 is a specific configuration on the fiber. Relative to some coordinates x^μ on shape space with origin at q_0 , we draw radial lines emanating from q_0 , that is, lines with coordinates $x^\mu(\lambda) = \lambda \xi^\mu$, where ξ^μ is a constant vector (a vector in the tangent space at q_0). The horizontal lifts of these lines, starting at Q_0 , sweep out the section \mathcal{S} of the Poincaré gauge. The condition $x^\mu \mathbf{A}_\mu = 0$ is equivalent to the condition that the fiber F above a

point q on a radial line is orthogonal to the lifted line in the section. This in turn is the condition for the horizontal lift. With this construction, the Poincaré gauge depends on the coordinates used to define the radial lines.

Now given the condition $x^\mu \mathbf{A}_\mu(x) = 0$, Eq. (3.9) follows. We prove this by writing

$$\mathbf{A}_\mu(x) = \int_0^1 dt \frac{d}{dt}(t\mathbf{A}_\mu) = \int_0^1 dt (\mathbf{A}_\mu + tx^\nu \mathbf{A}_{\mu,\nu}), \quad (3.12)$$

where all fields under the integral are evaluated at tx^μ . Then by using Eq. (3.8) to eliminate $\mathbf{A}_{\mu,\nu}$ in favor of $\mathbf{B}_{\mu\nu}$, then integrating by parts and using $x^\mu \mathbf{A}_\mu = 0$, we easily prove Eq. (3.9).

We can now use the non-Abelian version of Poincaré gauge to expand the gauge potential \mathbf{A}_μ about the equilibrium $x^\mu = 0$, and to express the result in terms of the curvature tensor $\mathbf{B}_{\mu\nu}$. The result is like Eq. (3.4):

$$\mathbf{A}_\mu(x) = \frac{1}{2}\mathbf{B}_{\alpha\mu} x^\alpha + \frac{1}{3}\mathbf{B}_{\alpha\mu,\beta} x^\alpha x^\beta + \dots, \quad (3.13)$$

where the fields on the right hand side are evaluated at equilibrium, $x^\mu = 0$. The gauge potential is expressed in terms of the Coriolis curvature form and its derivatives at equilibrium. Thus, the use of Poincaré gauge in the expansion of Eq. (2.13) and (2.14) simplifies the result and expresses it purely in terms of the Coriolis curvature tensor.

3.3 Riemann Normal Coordinates and the Eckart Conventions

However, the expansion of the Hamiltonian (2.14) still has quite a few terms in it, including those coming from an expansion of the metric tensor $g^{\mu\nu}$ about the equilibrium. The first derivatives of the metric tensor can be expressed in terms of the Christoffel symbols $\Gamma_{\alpha\beta}^\mu$ at equilibrium, the second derivatives in terms of the Riemann tensor $R^\mu{}_{\nu\alpha\beta}$, etc. The suggestion naturally arises that Riemann normal coordinates (Misner, Thorne and Wheeler [1973]) would simplify the expansion, certainly at least by making $\Gamma_{\alpha\beta}^\mu$ and therefore the derivatives of the metric tensor vanish at equilibrium. Further advantages are noted below.

To construct Riemann normal coordinates, we choose a fixed basis in the tangent space to shape space at q_0 , we let ξ^μ be the components of a tangent vector with respect to this basis, and we then construct the geodesics passing through q_0 with tangent vectors ξ^μ at parameter $\lambda = 0$. Then the point on a geodesic with parameter λ and initial tangent vector ξ^μ is assigned the Riemann normal coordinates $x^\mu = \lambda\xi^\mu$. Thus, radial lines in Riemann normal coordinates are geodesics. Since $d^2x^\mu/d\lambda^2 = 0$, we have the identity $\Gamma_{\alpha\beta}^\mu x^\alpha x^\beta = 0$ in Riemann normal coordinates. This reminds us of the condition $x^\mu \mathbf{A}_\mu = 0$ for Poincaré gauge.

In general, a geodesic on shape space is a trajectory $q(t)$ of a system of free particles with zero angular momentum, as is fairly obvious by setting $V = 0$ and $\mathbf{L} = 0$ in Eq. (2.12). The corresponding trajectory up in the bundle is of course a straight line with constant velocity, also with $\mathbf{L} = 0$. The bundle trajectory is also the horizontal lift of the trajectory in shape space (since $\mathbf{L} = 0$ is the condition for the horizontal lift). Thus, if Riemann normal coordinates are used to define the radial lines which when lifted produce the section for Poincaré gauge, that section will consist of all straight lines passing through a point Q_0

(see Fig. 5.1) on the equilibrium fiber F_0 which are orthogonal to F_0 at Q_0 . The section itself is then simply the flat subspace of \mathbb{R}^{3N-3} of dimension $3N - 6$ which is orthogonal to the equilibrium fiber F_0 at Q_0 (in fact, it passes through the origin and so is a vector subspace). But as explained in Littlejohn and Reinsch [1997], this is precisely the geometrical description of the Eckart frame (or gauge). Therefore the Eckart frame is the same as Poincaré gauge, relative to Riemann normal coordinates on shape space.

Eckart's conventions include not only a frame, but also a set of shape coordinates. These are constructed by first choosing a set of Euclidean coordinates with origin at Q_0 on the Eckart section, possible since it is a flat subspace of the bundle, itself a Euclidean space, and then projecting those onto shape space. Straight lines passing through the origin in these coordinates on the section are geodesics of zero angular momentum, which project onto radial geodesics on shape space. Thus, Eckart coordinates are Riemann normal coordinates. Furthermore, since the section is orthogonal to the equilibrium fiber, the metric on shape space at q_0 is the projection of the metric on the section at Q_0 , which means that the Eckart coordinates are orthonormal at q_0 . Often these coordinates are oriented so as to diagonalize $V_{,\mu\nu}$ at equilibrium, thereby transforming the unperturbed Hamiltonian into normal modes as in Eq. (2.18).

4 Expanding and Averaging the Hamiltonian

4.1 The Covariant Expansion of the Hamiltonian

We can now return to the expansion of the Hamiltonian (2.14), in which the potential V is already expanded and we must in addition expand the metric tensor $g^{\mu\nu}$, the inverse moment of inertia tensor M^{-1} , and the gauge potential A_μ . However, by Eq. (3.13), the latter is expressed in terms of the Coriolis curvature tensor, so we obtain the expansion of A_μ once that for $B_{\mu\nu}$ is known. These expansions by Taylor series produce coefficients which are the ordinary derivatives of these various tensor fields, evaluated at q_0 . Unfortunately, ordinary derivatives do not by themselves lead to covariant expressions, so we are motivated to reexpress all ordinary derivatives in terms of covariant derivatives of various tensor fields, including as it turns out the Riemann tensor, evaluated at q_0 . That this can be done at all is a special feature of Riemann normal coordinates and Poincaré gauge. The result, however, is a set of fully covariant expressions, valid in any coordinates or gauge.

We will omit the derivations of these expansions, and just quote the results. It is assumed that we are working in Riemann normal coordinates x^μ and Poincaré gauge. First, for the potential V , a scalar, it turns out that all ordinary derivatives are identical to covariant derivatives, when evaluated at $x^\mu = 0$. Thus, in this case, we can simply replace the comma by a semicolon, and the expansion of the potential is

$$V(x) = \sum_{n=0}^{\infty} \frac{1}{n!} V_{;\mu_1 \dots \mu_n}(0) x^{\mu_1} \dots x^{\mu_n}. \quad (4.1)$$

As for the metric tensor, its expansion in Riemann normal coordinates is discussed by Misner, Thorne and Wheeler [1973] and has been carried out to high order by Yamashita

[1984] with computer algebra. Through third order the result is

$$g^{\mu\nu}(x) = g^{\mu\nu}(0) - \frac{1}{3}R^\mu_{\alpha\beta}{}^\nu(0)x^\alpha x^\beta - \frac{1}{6}R^\mu_{\alpha\beta}{}^\nu{}_{;\gamma}(0)x^\alpha x^\beta x^\gamma + \dots, \quad (4.2)$$

where as noted above the first order terms vanish. As for the inverse moment of inertia tensor \mathbf{M}^{-1} and the Coriolis curvature tensor $\mathbf{B}_{\mu\nu}$, these are hybrid tensors, linking the tangent and cotangent spaces on shape space with the tangent spaces to the fibers (effectively the Lie algebra of $SO(3)$). Thus, the covariant derivatives of these tensors involves the gauge potential \mathbf{A}_μ as well as the Christoffel symbols $\Gamma^\mu_{\alpha\beta}$, as discussed by Littlejohn and Reinsch [1997]. As it turns out, the expansion of the inverse moment of inertia tensor is particularly simple:

$$\mathbf{M}^{-1}(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \mathbf{M}^{-1}_{;\mu_1 \dots \mu_n}(0) x^{\mu_1} \dots x^{\mu_n}, \quad (4.3)$$

very much like the expansion of V above. Finally, the gauge potential \mathbf{A}_μ has the following expansion, valid through third order,

$$\begin{aligned} \mathbf{A}_\mu(x) &= \frac{1}{2}\mathbf{B}_{\alpha\mu}(0)x^\alpha + \frac{1}{3}\mathbf{B}_{\alpha\mu;\beta}(0)x^\alpha x^\beta \\ &+ \left(\frac{1}{8}\mathbf{B}_{\alpha\mu;\beta\gamma}(0) + \frac{1}{12}R^\nu_{\alpha\beta\mu}(0)\mathbf{B}_{\gamma\nu}(0) \right) x^\alpha x^\beta x^\gamma + \dots \end{aligned} \quad (4.4)$$

4.2 The Perturbation Calculation

These expansions of the various fields allow us to write out the covariant expansion of the Hamiltonian, for which we write $H = \sum_n \kappa^n H_n$. In the following, it is understood that all fields, V , \mathbf{M}^{-1} , $g^{\mu\nu}$, $\mathbf{B}_{\mu\nu}$ and $R^\mu_{\nu\alpha\beta}$ and their derivatives, are evaluated at $x^\mu = 0$ (the equilibrium). The expansion through second order is given by

$$H_0 = \frac{1}{2}\mathbf{L} \cdot \mathbf{M}^{-1} \cdot \mathbf{L} + \frac{1}{2}p_\mu p^\mu + \frac{1}{2}V_{;\mu\nu} x^\mu x^\nu, \quad (4.5)$$

$$H_1 = \frac{1}{2}(\mathbf{L} \cdot \mathbf{M}^{-1}_{;\mu} \cdot \mathbf{L})x^\mu + \frac{1}{2}\mathbf{B}_{\mu\nu} p^\mu x^\nu + \frac{1}{6}V_{;\mu\nu\alpha} x^\mu x^\nu x^\alpha, \quad (4.6)$$

$$\begin{aligned} H_2 &= \frac{1}{4}(\mathbf{L} \cdot \mathbf{M}^{-1}_{;\mu\nu} \cdot \mathbf{L})x^\mu x^\nu + \frac{1}{3}(\mathbf{L} \cdot \mathbf{B}_{\mu\alpha;\beta})p^\mu x^\alpha x^\beta + \frac{1}{6}R_{\mu\alpha\nu\beta} p^\mu p^\nu x^\alpha x^\beta \\ &+ \frac{1}{8}(\mathbf{L} \cdot \mathbf{B}_{\alpha\mu})(\mathbf{L} \cdot \mathbf{B}_{\beta}{}^\mu)x^\alpha x^\beta + \frac{1}{24}V_{;\mu\nu\alpha\beta} x^\mu x^\nu x^\alpha x^\beta. \end{aligned} \quad (4.7)$$

Some further simplification of this expansion can be achieved by using the Kaluza-Klein identities for the N -body problem, which are given by Littlejohn and Reinsch [1997]. However, we have found that the results of the averaging transformation, Eq. (4.10), seem to be simpler if we leave the expanded Hamiltonian as it is. We remark that the Kaluza-Klein identities show that all the fields which occur in the expansion of the Hamiltonian (not counting V), plus all of their covariant derivatives, can be expressed in terms of just the three fields \mathbf{M} , $\mathbf{M}_{;\mu}$ and $\mathbf{B}_{\mu\nu}$. Indeed, such a reduction is necessary to reconcile the covariant expansion we have developed with the standard, noncovariant expansion of the Watson Hamiltonian (see, for example, Papoušek and Aliev [1982]).

We now assume that the Riemann normal coordinates are chosen to be orthogonal (they are now Eckart coordinates) and to diagonalize $V_{;\mu\nu}$, as in Eq. (2.18). Thus, $g_{\mu\nu} = \delta_{\mu\nu}$ at equilibrium. For simplicity we also assume that the frequencies of small vibrations are nondegenerate, or more precisely, that $\{\omega_\mu\}$ are rationally independent and sufficiently far from resonance. Many common molecules are highly symmetric and have degenerate frequencies of vibration, so this condition does not hold for them. See Harter [1993] for an analysis of this case. We next introduce action angle variables,

$$x^\mu = \sqrt{\frac{2I_\mu}{\omega_\mu}} \sin \theta_\mu, \quad p_\mu = \sqrt{2I_\mu \omega_\mu} \cos \theta_\mu, \quad (4.8)$$

and finally carry out the averaging transformation. It turns out that the slow Poisson bracket (the second term in Eq. (2.16)) does not contribute to the result at second order (it occurs in the expansion, but averages to zero).

The results of the expansion to second order are the following. We write $K = \sum_n \kappa^n K_n$. We have

$$K_0 = \frac{1}{2} \mathbf{L} \cdot \mathbf{M}^{-1} \cdot \mathbf{L} + \sum_\mu I_\mu \omega_\mu, \quad (4.9)$$

and $K_1 = 0$. For the second order Hamiltonian, we find

$$\begin{aligned} K_2 = & \frac{1}{4} \sum_{\mu \neq \nu} (\mathbf{L} \cdot \mathbf{B}_{\mu\nu})^2 \frac{I_\mu \omega_\mu - I_\nu \omega_\nu}{\omega_\mu^2 - \omega_\nu^2} + \frac{1}{12} \sum_{\mu\nu} R_{\mu\nu\mu\nu} I_\mu I_\nu \left(\frac{\omega_\mu}{\omega_\nu} + \frac{\omega_\nu}{\omega_\mu} \right) \\ & + \frac{1}{4} \sum_\mu (\mathbf{L} \cdot \mathbf{M}_{;\mu\mu}^{-1} \cdot \mathbf{L}) \frac{I_\mu}{\omega_\mu} - \frac{1}{8} \sum_\mu \frac{1}{\omega_\mu^2} \left(\mathbf{L} \cdot \mathbf{M}_{;\mu}^{-1} \cdot \mathbf{L} + \sum_\nu V_{;\nu\nu\mu} \frac{I_\nu}{\omega_\nu} \right)^2 \\ & - \frac{1}{48} \sum_{\mu\nu\sigma} \frac{V_{;\mu\nu\sigma}^2}{\omega_\mu \omega_\nu \omega_\sigma} \left[\frac{I_\nu I_\sigma + I_\mu I_\sigma + I_\mu I_\nu}{\omega_\mu + \omega_\nu + \omega_\sigma} + \frac{I_\nu I_\sigma + I_\mu I_\sigma - I_\mu I_\nu}{\omega_\mu + \omega_\nu - \omega_\sigma} \right. \\ & \quad \left. + \frac{I_\nu I_\sigma - I_\mu I_\sigma + I_\mu I_\nu}{\omega_\mu - \omega_\nu + \omega_\sigma} + \frac{-I_\nu I_\sigma + I_\mu I_\sigma + I_\mu I_\nu}{-\omega_\mu + \omega_\nu + \omega_\sigma} \right] \\ & - \frac{1}{16} \sum_{\mu\nu} \frac{V_{;\mu\mu\nu}^2}{\omega_\mu^2} \frac{I_\mu^2}{4\omega_\mu^2 - \omega_\nu^2} + \frac{1}{8} \sum_{\mu\nu} \frac{V_{;\mu\mu\nu}^2}{\omega_\mu^2 \omega_\nu^2} I_\mu^2 \\ & + \frac{1}{8} \sum_{\mu\nu} V_{;\mu\nu\mu\nu} \frac{I_\mu I_\nu}{\omega_\mu \omega_\nu} - \frac{1}{16} \sum_\mu V_{;\mu\mu\mu\mu} \frac{I_\mu^2}{\omega_\mu^2}. \end{aligned} \quad (4.10)$$

Most of the work in deriving this result, and the most complicated parts of the result, come from averaging the cubic and quartic contributions to the potential. These terms have nothing to do with the gauge fields or the curvature of the manifold (they would be present in a multidimensional generalization of Eq. (2.3) on a flat space), and so are relatively uninteresting from the standpoint of the geometry of the fiber bundle. But even if we are only interested in those terms which have a dependence on the angular momentum or the curvature tensors, we cannot ignore the potential, because there is a nonlinear beating between the cubic contributions to the potential and the centrifugal distortion, which is seen

in fourth major sum. Terms of this sort are also present in the diatomic result, Eq. (2.8), which in fact is a special case of Eq. (4.10).

The first sum in Eq. (4.10) is the contribution from the Coriolis forces, and is an obvious non-Abelian generalization of the result found in Eq. (3.7) for the oscillator in the magnetic field. The second sum represents the sampling of the curvature of shape space by the oscillator. The third sum obviously involves the second order effects of the centrifugal distortion of the moment of inertia tensor. Nonlinear beatings of the first order centrifugal distortion of the moment of inertia tensor with itself are seen in the fourth major sum, which produces a term quartic in the angular momentum.

The vibrational actions I_μ are formal invariants of this Hamiltonian, which effectively is reduced to one degree of freedom, that of the angular momentum \mathbf{L} . For fixed values of the actions I_μ , the Hamiltonian is an even quartic in the angular momentum \mathbf{L} (sixth and higher order terms would appear in higher order perturbation theory). Thus, the dynamics of \mathbf{L} on the angular momentum sphere can display a much richer set of oscillations and separatrices than in the case of a rigid body (where H is only a quadratic function of \mathbf{L}). This is an old and well studied theme in molecular physics.

The results of a quantum calculation are quite close to the classical result given above, mainly because of the strong similarity between classical and quantum harmonic oscillator theory. Thus, a very good idea of the correct quantum result is obtained by replacing I_μ above by $(n_\mu + 1/2)\hbar$, where n_μ is the quantum number of the μ -th normal mode. The result is then a quantum Hamiltonian in the angular momentum alone, which can be solved either by diagonalizing the $(2\ell + 1) \times (2\ell + 1)$ dimensional matrix for H , or by semiclassical (Bohr-Sommerfeld) methods on the angular momentum sphere.

The effect of the averaging transformation is to create a collection of tensors, defined on the tangent space to shape space at q_0 , whose components are simple in the orthonormal frame of the normal modes of the potential. For example, in the third major sum in Eq. (4.10) there occurs a tensor with components $(I_\mu/\omega_\mu)\delta_{\mu\nu}$. The final result can be expressed in terms of generally covariant contractions with these tensors.

5 Conclusions

We will conclude with the following suggestion for a generalization of this work. Molecular clusters are currently an active area of research. Such clusters are often modelled as a collection of rigid bodies, interacting by some potential. In this model, the Hamiltonian for a cluster is a generalization of Eq. (2.12), in that the “particles” are no longer points, but rather have their own (fixed) moment of inertia tensors and rotational kinetic energy. We have recently worked out this Hamiltonian in general form (Mitchell and Littlejohn [1999]). Suppose we wish to study rovibrational coupling in such systems. How are the Eckart frame and coordinates to be generalized? There is no clue from Eckart’s original (coordinate-based) definition. However, the analysis above shows that the coordinates should be Riemann normal coordinates, which are constructed out of radial geodesics (potential free motions of zero angular momentum), whose horizontal lifts define the section for a version of Poincaré gauge. In this case, the potential free motion no longer consists of straight lines (the free rotation of asymmetric tops is somewhat nontrivial). Nevertheless, the covariant Taylor series expansions developed above can be carried over almost without modification. We will

report on these developments in the future.

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Figure Captions

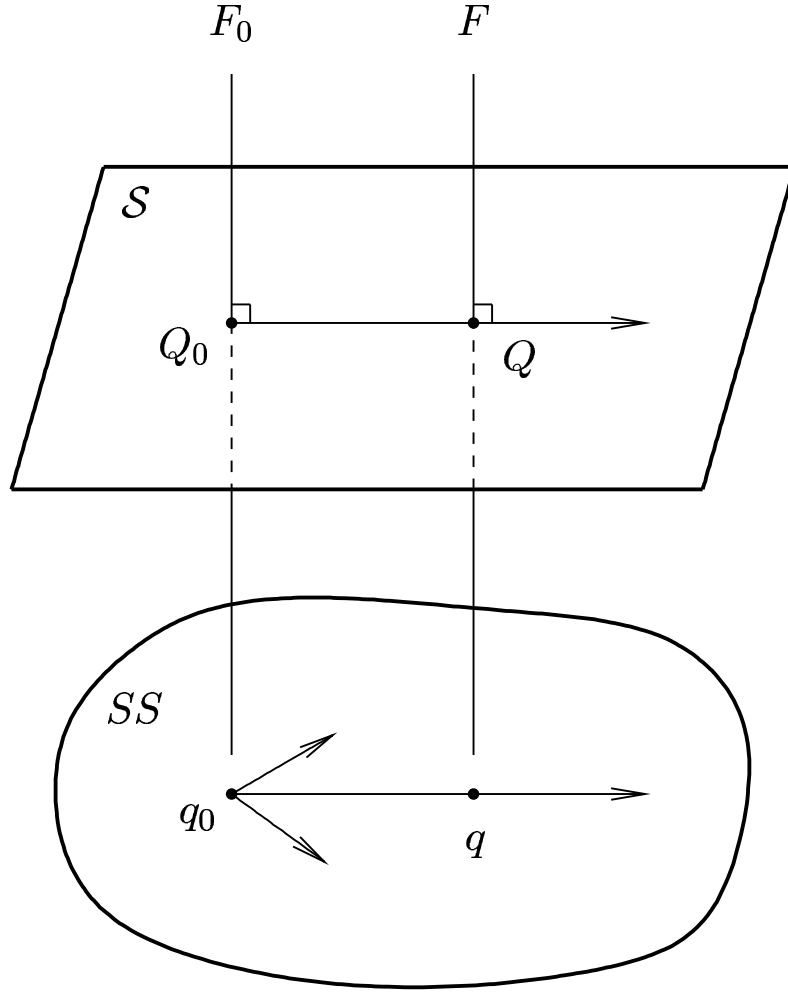


Figure 5.1: Poincaré gauge can be described as the section which is the horizontal lift of radial lines emanating from the equilibrium shape q_0 . The lines are radial in some coordinate system with origin at q_0 . If Riemann normal coordinates are used, the section is flat and coincides with the section of the Eckart frame.