Monopole Gauge Fields and Quantum Potentials Induced by the Geometry in Simple Dynamical Systems

P. Maraner
Dipartimento di Fisica, Università di Parma, and INFN, Gruppo collegato di Parma, Viale delle Scienze, 43100 Parma, Italy

May 1994

Abstract

A realistic analysis shows that constraining a quantomechanical system produces the effective dynamics to be coupled with abelian/non-abelian gauge fields and quantum potentials induced by the intrinsic and extrinsic geometrical properties of the constraint’s surface. This phenomenon is observable in the effective rotational motion of some simple polyatomic molecules. By considering specific examples it is shown that the effective Hamiltonians for the nuclear rotation of linear and symmetric top molecules are equivalent to that of a charged system moving in a background magnetic-monopole field. For spherical top molecules an explicit analytical expression of a non-abelian monopole-like field is found. Quantum potentials are also relevant for the description of rotovibrational interactions.
1 Introduction

One of the first questions addressed by researchers who first studied the properties of surfaces embedded in the three-dimensional euclidean space, at the beginning of nineteenth century, may be formulated more or less in this terms:

Is it possible for an hypothetical inhabitant of a surface embedded in the three-dimensional euclidean space to completely reconstruct the geometrical features of his world by performing physics experiment?

At that time physics consisted essentially in Newtonian mechanics. It was soon realized that the free motion of a particle on a surface only depends on what are today called the intrinsic geometric properties. That is, it results completely insensible to the way in which the surface is embedded in $\mathbb{R}^3$, that is on its extrinsic geometric properties. As a typical example it is very easy to be convinced that classical dynamics on a cone or on a cylinder in locally undistinguishable from that on a plane. Once recognizing that constraining a dynamical system corresponds to reducing the motion from the $n$-dimensional euclidean space $\mathbb{R}^n$ to a submanifold, it appears evident that the extension of this beautiful results to arbitrary submanifold of $\mathbb{R}^n$ lies at the heart of the classical theory of constrained system. It constitutes the geometrical meaning of d’Alambert’s principle.

Almost two century later we readdress the same question, extended to arbitrary submanifold of $\mathbb{R}^n$, in the realm of quantum mechanics. In pursuing this goal it is necessary to overcome the prejudice generated by the classical results, that is, dynamics only depends on constraint’s intrinsic geometry. On the contrary quantum mechanics is very sensitive on extrinsic geometry, which appears in the effective constrained dynamics by means of the coupling with gauge fields and quantum potentials [1]. The first contribution to this theory has been given by H. Jensen and H. Koppe [2] who studied the problem of a quantum particle constrained on a surface in $\mathbb{R}^3$ in a realistic way. The case of a wire in $\mathbb{R}^3$ has also been treated by many authors [3] and discussed
in definitive form by S. Takagi and T. Tanzawa [4]. After many attempts [5] the problem for an arbitrary submanifold of \( R^n \) has been finally solved independently by K. Fujii and N. Ogawa [6] and P. M. and C. Destri [1] laying the theoretical foundation of a quantum theory of holonomic constraint.

Besides the mathematical interest of this theory it is important to understand whether this results are physically significant, that is whether geometry induced gauge fields and quantum potentials appearing in the effective constrained dynamics lead to some observable phenomenon. This is the main aim of this paper. The answer that I will give is somewhat surprising, showing that effect connected with abelian and non-abelian monopole gauge fields and quantum potentials already has been observed in physics at the beginning of the thirty’s [7], that is at the time of Dirac’s paper [8] on magnetic monopole and twenty-five years before the work in which Yang and Mills introduced the concept of non-abelian gauge field [9]. A similar situation has also been found in the context of geometric phase [10, 11]. The mechanism which produces the coupling with gauge fields in constrained quantum mechanics is however distinct from that explored by M. V. Berry, B. Simon and F. Wilczek and A. Zee [12]. In this paper I consider simple dynamical models of some polyatomic molecules giving a new analysis of the rigid body approximation allowing the separation of vibrational and rotational nuclear coordinates. Electronic degrees of freedom are supposed to be separated by means of the Born-Oppenheimer approximation and attention is focused on nuclear motion only. The “rigid body” is considered in the light of the quantum treatment of holonomic constraint recently developed in Ref. [1], showing how rotovibrational interactions for symmetrical molecules known as Coriolis interactions [13, 14], are taken into account in the effective rotational dynamics by means of the coupling with gauge fields and quantum potentials induced by the constraint. This illustrates the general geometrical mechanism producing Coriolis coupling, giving at one time a powerful method to compute them and an observable example of gauge structures and quantum potentials induced in constrained quantum mechanics.

The paper is organized as follows. In section 2, I address the problem of holonomic constraint in quantum mechanics by discussing the physical meaning of considering the motion of a quantum system on a surface in \( R^3 \) or more generally on a submanifold of \( R^n \). I do this by considering a specific example. The fundamental difference between constrained classical and quantum mechanics is then outlined and a general definition of a con-
strained quantum system is given in terms of a microscopic potential. The effective quantum dynamics on the constraint is discussed in section 3. After adapting coordinates and introducing the geometrical quantities characterizing the constraint’s surface, it is shown how the general hypothesis on the microscopic nature of the constraint allow to set up a perturbative description of the motion of the system. The effective quantum dynamics results covariant in character and depends on extrinsic geometry by means of the coupling with gauge fields and quantum potentials.

The theory is applied to simple molecular systems in sections 4, 5, 6 and 7. Exploring the rigid body model of some polyatomic molecules in the light of the theory developed in section 3, it is shown how monopole gauge fields and quantum potentials induced by the rigidity constraint are responsible for long studied rotovibrational interactions.

2 Constraints in Quantum Mechanics

Among the topics which have most attracted the interest of physicists in the last decade the study of bidimensional systems plays certainly an important role. Although in many cases the two dimensions are considered in toy models, in others we are faced with real systems whose dynamics appears to be effectively bidimensional. A very important example is found in the description of Quantum Hall Effect, explained by means of the properties of a bidimensional electron gas. Let us consider the physical mechanism realizing planarity. Quantum Hall Effect is observed in inversion layers in presence of a strong magnetic field and at very low temperatures. Inversion layers, in which the planarity constraint is realized, are formed at the interface between a semiconductor and an insulator. When a potential difference is applied an electric field normal to the interface attracts the free electrons from the semiconductor to the interface itself. The motion normal to the interface is then confined in a potential well while the motion in other directions may be considered free. In a free electron approximation, relevant for Integer Quantum Hall Effect, the dynamics separates and the energy of each electron may be decomposed in a term relative to the normal motion, $E^{nor}$, and one
relative to the motion along the interface, $E^{\text{tan}}$,

$$E = E^{\text{nor}} + E^{\text{tan}}.$$  

The deeper the potential well confining the particle the greater $E^{\text{nor}}$ with respect to $E^{\text{tan}}$. The spectrum of the system separates in bands. In correspondence of every normal eigenstate the whole spectrum of the motion along the interface may be observed. The ideal situation to investigate the Quantum Hall Effect is that in which only the first band is occupied and it is indeed possible to arrange the experimental apparatus in such a way. In any physical realization of the planarity constraint it is however necessary to take into account the whole band spectrum. In reducing the motion of a quantum system from $R^3$ to the plane $R^2$ is therefore possible to separate the degrees of freedom normal to the constraint to that along it obtaining an effective bidimensional dynamics. The whole spectrum keeps nevertheless memory of the way this has been done. The energies are in first approximation those corresponding to the interface’s potential $V_I$ and different shapes of $V_I$ produces different band structures.

The analysis of this simple example shades light on the fundamental difference between the classical and quantum nature of constraints. Whereas the classical system may be completely squeezed on the constraint’s surface ignoring motion in normal directions, Heisemberg’s principle forbids this operation in the quantum case. The more the system is squeezed on the constraint’s surface the more relevant the motion in normal directions. In describing a quantum system we can’t therefore ignore the physical mechanism realizing a constraint, that is the explicit form of the confining potential $V_C$. The example of inversion layers suggest that two general properties have to be satisfied by $V_C$

1) $V_C$ presents a deep minimum in correspondence of the constraint’s surface

2) $V_C$ depends only on coordinates normal to the constraint’s surface

In next section I will show how is possible to separate the motion along and normal to a generic constraint and how the induced dynamics depends on the explicit form of $V_C$. 

5
3 Effective Quantum Dynamics

As usual, in addressing the solution of a physical problem the choice of coordinates adapted to the system under consideration is of fundamental importance. In the sequel we consider an arbitrary $m$-dimensional submanifold $M$ of the euclidean space $R^n$. Everywhere the attribute tangent and normal are referred to $M$. To adapt coordinates we introduce

— a coordinate frame $\{x^\mu; \mu = 1,...,m\}$ on $M$, or, equivalently a smooth assignation of $m$ independent tangent vectors $t_\mu(x)$, $\mu = 1,...,m$,

— a choice of $(n-m)$ smooth varying orthonormal normal vectors $n^i(x)$, $i = m+1,...,n$, and associated to it, the distances $\{y^i; i = m+1,...,n\}$ along the geodetics leaving $M$ with speed $n^i$.

The set $\{x^\mu, y^i; \mu = 1,...,m, i = m+1,...,n\}$ constitutes a good coordinate system for $R^n$ at least in a sufficiently small neighbourhood of $M$. The submanifold $M$ may be completely characterized in terms of the quantities

\[
g_{\mu\nu} = t_\mu \cdot t_\nu \quad \text{metric (first fundamental form)}
\]

\[
\alpha^i_{\mu\nu} = t_\mu \cdot \partial_\nu n^i \quad \text{second fundamental form}
\]

\[
A^{ij}_\mu = n^i \cdot \partial_\mu n^j \quad \text{normal fundamental form}
\]

where $\partial_\mu = \frac{\partial}{\partial x^\mu}$ and the dot denotes the scalar product in $R^n$. $g_{\mu\nu}$ describes the intrinsic properties of $M$ whereas $\alpha^i_{\mu\nu}$ and $A^{ij}_\mu$ its extrinsic geometry. As an example consider an arc-length parameterized curve embedded in $R^3$ with $n^2$, $n^3$ chosen as normal and binormal. Then we obtain: $g_{11} = 1$, reflecting the fact that intrinsic geometry of a one-dimensional manifold is always trivial; $\alpha^2_{11} = k$, the curve’s curvature, $\alpha^3_{11} = 0$ and $A^{23} = -A^{32} = \tau$, the curve’s torsion.

The metric $G_{IJ}$ of $R^n$ in the adapted coordinates frame $\{x^\mu, y^i\}$ is written solely in terms of $g_{\mu\nu}$, $\alpha^i_{\mu\nu}$ and $A^{ij}_\mu$ as

\[
G_{IJ} = \begin{pmatrix}
g_{\mu\nu} + y^k y^l A^{kh}_\mu A^{lh}_\nu & y^k A^{jk}_\mu \\
y^k A^{ik}_\nu & \delta^{ij}_\mu
\end{pmatrix},
\]

(1)
where $\gamma_{\mu\nu} = g_{\mu\nu} - 2y^k\alpha^k_{\mu\nu} + y^k y^l \alpha^k_{\mu\rho} g^{\rho\sigma} \alpha^l_{\sigma\nu}$. It is important to note that the variation of the $n^i(x)$'s by a point dependent rotation $R^{kl}(x)$ produces $A^{ij}_\mu$ to transform as an $SO(n - m)$ gauge potential

$$A^{ij}_\mu \rightarrow R^{ik}_\mu A^{kl}_\mu R^{jl}_\mu + R^{ik}_\mu \partial_\mu R^{jk}.$$ 

The characterization of a constraint by means of a potential satisfying the general conditions given in the previous section and the choice of adapted coordinates allows to give a complete description of the constrained dynamics. To achieve this aim

— We start by unambiguously quantizing the system in a cartesian coordinate frame $\{r^I; I = 1, ..., n\}$ of $R^n$. The Hamiltonian reads

$$\mathcal{H} = -\frac{1}{2} \sum_{I=1}^{n} \frac{\partial^2}{\partial r^I^2} + V_C. \quad (2)$$

— Then we transform to adapted coordinates obtaining the Hamiltonian’s expression

$$\mathcal{H} = -\frac{1}{2G^{1/2}} \partial_I G^{IJ} G^{1/2} \partial_J + V_C, \quad (3)$$

where $G$ and $G^{IJ}$ denote respectively the determinant an the inverse of the metric tensor $G_{IJ}$. For a review of quantum mechanics in an arbitrary coordinates frame see Ref.[13]. Everywhere in this paper the sum over repeated index is understood.

— Performing the similitude transformation

$$\mathcal{H} \rightarrow \frac{G^{1/4}}{g^{1/4}} \mathcal{H} \frac{g^{1/4}}{G^{1/4}} \quad (4)$$

we obtain an Hamiltonian acting on wavefunction which are correctly normalized on the submanifold $M$.

---

1In this section $\hbar = 1$ and masses are supposed to be reabsorbed in the relative coordinates.
— At this point, and only at this point, we implement conditions $C1$ and $C2$ by expanding $V_C$ around its minimum

$$V_C = \frac{1}{2\epsilon^2} \omega^i y^i y^i + a_{ijk} y^i y^j y^k + b_{ijkl} y^i y^j y^k y^l + \ldots,$$

where the scale of the frequencies $\omega^i$ has been reabsorbed in the adimensional parameter $\epsilon^{-1}$. The smaller $\epsilon$ the more the system is squeezed on the constraint’s surface.

— $\epsilon$ appears as a natural perturbative parameter in the theory. Rescaling the normal coordinates by $\bar{y} \rightarrow \epsilon^{1/2} \bar{y}$ the Hamiltonian may be expanded in powers of $\epsilon$ as

$$\epsilon \mathcal{H} = H^{(0)} + \epsilon H^{(1)} + \epsilon^{3/2} H^{(3/2)} + \ldots + \epsilon^{5/2} a_{ijk} y^i y^j y^k + \epsilon^3 b_{ijkl} y^i y^j y^k y^l + \ldots.$$

As for the planarity constraint discussed in the second section the zero order Hamiltonian $H^{(0)}$ depends only on normal degrees of freedom. It describes a system of $(n - m)$ uncoupled harmonic oscillators with frequencies $\omega^{m+1}, \ldots, \omega^n$,

$$H^{(0)} = \frac{1}{2} \left( -\partial_i \partial_i + \omega^2 y^i y^i \right).$$

The first order terms $H^{(1)}$, to which I will restrict the analysis in this paper, describes the effective dynamics on the constraint. It is covariant in character and coupled to the normal dynamics by means of the minimal interaction with a geometry induced gauge field and a quantum potential

$$H^{(1)} = -\frac{1}{2g^{1/2}} \left( \partial_\mu + \frac{i}{2} A_\mu L_{ij} \right) g^{\nu \rho} g^{1/2} \left( \partial_\nu + \frac{i}{2} A_\nu A_{kl} \right) + Q(x)$$

where $L_{ij} = -i(y^i \partial_j - y^j \partial_i)$ are angular momentum operators in the normal directions and the potential $Q(x)$ may be expressed in terms of the intrinsic scalar curvature $R$ and the extrinsic mean curvature $\eta$ of $M$ as

$$Q(x) = \frac{1}{4} R(x) - \frac{m^2}{8} \eta^2(x).$$
Second, third and following terms of the \( V_C \)'s expansion may be of the same order than \( H^{(1)} \) and have eventually to be considered together in addressing the perturbation theory. Higher orders terms, \( H^{(3/2)}, H^{(2)}, \ldots \) describe the interactions between normal and tangent degrees of freedom \[21\].

To separate definitively the dynamics on \( M \) from that normal to \( M \) we proceed by means of standard perturbation theory. Let us label with \( E^{(0)} = \sum_i \omega^i(n_i + 1/2) \) the, possibly degenerate, states of \( H^{(0)} \). In correspondence of every \( E^{(0)} \) the corrections to the spectrum have to be evaluated by diagonalizing the perturbation, that is by solving the Schrödinger equation corresponding to Hamiltonian

\[
H^{E^{(0)}} = -\frac{1}{2g^{1/2}} (\partial_\mu + iA_\mu) g^{\mu\nu} g^{1/2} (\partial_\nu + iA_\nu) + Q(x) + \bar{Q}(x) \tag{10}
\]

with

\[
A_\mu = \frac{1}{2} A^{ij}_\mu \langle L_{ij} \rangle, \tag{11}
\]

\[
\bar{Q}(x) = \frac{1}{8} g^{\mu\nu} A^{ij}_\mu A^{kl}_\nu (\langle L_{ij} L_{kl} \rangle - \langle L_{ij} \rangle \langle L_{kl} \rangle), \tag{12}
\]

where \( \langle L_{ij} \rangle \) and \( \langle L_{ij} L_{kl} \rangle \) denote the matrices obtained by bracketing \( L_{ij} \) and \( L_{ij} L_{kl} \) between the eigenstates corresponding to \( E^{(0)} \). \( H^{E^{(0)}} \) describe the effective motion on the submanifold when the normal degrees of freedom are frozen in the state \( E^{(0)} \). \( \langle L_{ij} \rangle \) results different from zero if and only if \( V_C \) posses degenerate frequencies, this being the condition for the coupling with gauge fields not to disappear. Moreover, if a frequency has degeneracy \( d \) the \( \langle L_{ij} \rangle \)'s with \( i \) and \( j \) corresponding to that frequency form a matrix representation of the generators of \( SO(d) \). Denoted by \( \omega_1, \ldots, \omega_r \) the distinct proper frequencies of \( V_C \) and by \( d_1, \ldots, d_r, d_1 + \ldots + d_r = n - m \), their degeneracies, the geometry induced gauge group of the theory is \( SO(d_1) \times \ldots \times SO(d_r) \).

As a particular case we may recover the Jensen-Koppe answer to the question proposed in the introduction. The Hamiltonian describing the effective motion of a quantum particle constrained on a surface embedded in \( R^3 \) is given by

\[
\mathcal{H} = -\frac{1}{2} \Delta - \frac{1}{4} \left( \frac{1}{R_1} - \frac{1}{R_2} \right)^2 \tag{13}
\]

where \( \Delta \) is the Laplacian on the surface and \( R_1 \) and \( R_2 \) its principal radii of curvature. In this simple example the dynamics does not depends on the
normal state and the coupling with geometry induced gauge fields disappears. The drastic difference with the classical case may nevertheless be observed by considering the motion on a cone. Whereas the classical particle behaves as free the quantum particle is attracted on the vertex from a quantum potential \[16\]. The simpler case in which dynamics results coupled with geometry induced gauge fields is the wire embedded in \(R^3\) as discussed by S. Takagi and T. Tanzawa \[4\].

A realistic analysis of constrained quantum systems shows the emergence of a rich dynamical structure unexpected from semiclassical considerations and it is a wonderful surprise to rediscover abelian an non-abelian gauge structures in a so simple dynamical context. This phenomenon very much resemble Berry’s analysis of the adiabatic approximation \[17\] and considering the motion on the constraint by freezing normal degrees of freedom is an adiabatic approximation after all. Nevertheless the mechanism producing the coupling with gauge fields in constrained quantum mechanics is different from that considered by M. V. Berry. In the context of Berry’s geometric phase the embedding of the slow coordinates space in the total configuration space is trivial, whereas this non-triviality lies at the heart of the mechanism appearing in the treatment of constraint.

4 Molecules as Constrained Systems

Extremely important examples of constrained systems in quantum mechanics are given by molecular physics. The description of molecular spectra \[18\] starts from the many-body Hamiltonian given by the sum of electronic and nuclear kinetic energy plus the coulomb interaction between all the particles. At this point electronic and nuclear degrees of freedom are separated by means of the Born-Oppenheimer approximation and an effective Hamiltonian describing the nuclear motion is obtained

\[
\mathcal{H}_{\text{nuc}} = - \sum_{a=1}^{N} \frac{\hbar^2}{2m_a} \frac{\partial^2}{\partial \vec{r}_a^2} + V_{BO},
\]

(14)

where \(\vec{r}_a\), \(a = 1, \ldots, N\), denotes the coordinates of the \(a\)-th nucleus, \(m_a\) its mass, and \(V_{BO}\) the Born-Oppenheimer potential. For sake of clearness I
will ignore throughout this paper eventual effects connected to the geometric phase. \( V_{BO} \) presents a deep minimum in correspondence of the equilibrium configuration of the molecule. Since this is determined up to orientation in space, that is, up to an \( SO(3) \) rotation, the previous sentence may be rephrased by saying

— \( V_{BO} \) presents a deep minimum in correspondence of the submanifold \( SO(3) \) of the nuclear configuration space \( R^{3N-3} \).

Nuclear positions are referred to the body center frame. Depending only on relative nuclear distances, \( V_{BO} \) does not depend on molecule’s orientation in space, that is to say

— \( V_{BO} \) depends only on coordinates normal to the submanifold \( SO(3) \) of the nuclear configuration space \( R^{3N-3} \).

These are exactly conditions \( C1 \) and \( C2 \) introduced in the second section to describe a potential realizing a constraint. The Born-Oppenheimer potential \( V_{BO} \) realizes therefore a rigidity constraint\(^2\) confining the nuclear motion from the configuration space \( R^{3N-3} \) to the rotational group \( SO(3) \).

The use a rigid body model to separate vibrational and rotational degrees of freedom is a standard matter \[18\]. Nevertheless the rigidity constraint always has been understand in a classical fashion without catching the general structure underlying it. In next sections I will show how Coriolis interaction and other features of polyatomic molecular spectra may be described by means of geometry induced abelian and non-abelian monopole gauge fields and quantum potentials appearing in the effective rotational dynamics.

For the moment let me prepare the way by adapting coordinates to \( SO(3) \). We introduce a cartesian frame xyz fixed in the equilibrium configuration of the molecule. For sake of simplicity we shall choose it as a principal frame of inertia. The unit vectors \( e_x, e_y, e_z \) along x, y and z will be expressed in terms of the three Euler angles \( \alpha, \beta, \gamma \) parametrizing the rotational group \( SO(3) \) and the position of the \( a \)-th nucleus in the xyz frame is specified by \( \vec{r}_a = (x_a, y_a, z_a), \ a = 1, ..., N, \) which is thought as function of the normal coordinates \( \xi_i, i = 1, ..., 3N - 6, \) of the potential. It is easy to be convinced that \( \{\alpha, \beta, \gamma, \xi_1, \xi_2, ..., \xi_{3N-6}\} \) constitutes an

\(^2\)In the least decade there has been a growing interest in the study of non-rigid molecules \[13\]. Following considerations do not apply to these systems.
adapted coordinates frame in the sense specified before. The transformation \( (\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \rightarrow (\alpha, \beta, \gamma, \xi_1, \xi_2, ..., \xi_{3N-6}) \) takes the form
\[
\vec{r}_a = x_a(\vec{\xi})e_x + y_a(\vec{\xi})e_y + z_a(\vec{\xi})e_z
\] (15)
for \( a = 1, ..., N \). Treating the constraint as in section 3 we obtain the effective rotational dynamics to be described by Hamiltonian (10), which is completely characterized by the geometric quantities describing the embedding of SO(3) in \( R^{3N-3} \). The indexes \( \mu, \nu \) run now over 1 to 3 and label the three Euler angles. \( g^{\mu\nu} \) is the inverse of the rigid body metric on \( SO(3) \)
\[
g_{11} = (I_X \cos^2 \gamma + I_Y \sin^2 \gamma) \sin^2 \beta + I_Z \cos^2 \beta,
\]
\[
g_{12} = g_{21} = (I_Y - I_X) \sin \beta \sin \gamma \cos \gamma,
\]
\[
g_{13} = g_{31} = I_Z \cos \beta,
\]
\[
g_{22} = I_X \sin^2 \gamma + I_Y \cos^2 \gamma,
\]
\[
g_{23} = g_{32} = 0,
\]
\[
g_{33} = I_Z,
\]
where \( I_X, I_Y, I_Z \) are the principal moments of inertia of the molecule. The explicit form of the normal fundamental form \( A^{ij}_{\mu} \) depends on the system under consideration and will be given in the sequel for some classes of molecules. Finally for every electronic configuration the potential \( Q(\alpha, \beta, \gamma) \) results to be a constant expressed in terms of the inertia tensor \( I \) as
\[
Q = \hbar^2 \frac{\text{tr} \left( I^2 \right) - \left( \text{tr} \ I \right)^2}{2 \det I}.
\] (16)

A quick look to Eqs. (10), (11) and (12) illustrates very clearly and concisely how rotational motion couples with molecular vibrations. Effects connected with geometry induced gauge fields are expected for molecules presenting degenerate proper frequencies, while the quantum potential (12) produces a rotovibrational coupling even in the non-symmetrical case. To appreciate the difference with the standard treatment of the rigidity constraint compare Hamiltonian (10) with Eq. (III.2) of the classical report Ref. [20]. The gauge field (11) and the quantum potential (12) are neglected in the rotational Hamiltonian and considered only as perturbative corrections.
5 Monopoles, Quantum Potentials and the linear symmetric $XY_2$ molecule

Let me start by briefly recalling the semiclassical picture describing the rotovibrational spectrum of the linear symmetric $XY_2$ molecule. In first approximation $XY_2$ is thought as a rigid dumbbell capable to perform small vibrations around its equilibrium position and to rotate around its body center. Rotational energies are described by that of a spherical top

$$E_{\text{rot}} = \frac{\hbar^2}{2I}(l + 1),$$

(17)

$I$ being the momentum of inertia. The quantum number $l$ may in principle assume every positive integer values $l = 0, 1, \ldots$ Molecular vibrations may be described in terms of four uncoupled harmonic oscillators by adapting normal coordinates. Since $\omega_2$ is doubly degenerate vibrational energies may be written in terms of three quantum numbers $n_1, n_2, n_3 = 0, 1, \ldots$ as

$$E_{\text{vib}} = \hbar \omega_1(n_1 + 1/2) + \hbar \omega_2(n_2 + 1) + \hbar \omega_3(n_3 + 1/2).$$

(18)

The $XY_2$ spectrum is then expected to be described in rough approximation by the sum of vibrational and rotational energies

$$E = E_{\text{vib}} + E_{\text{rot}}$$

(19)

and in fact, apart from the absence of some values of $l$, it is so. In order to justify the absences is necessary to remember that in a many-body system is not possible in general to completely separate rotational and vibrational degrees of freedom. When normal modes corresponding to the degenerate frequency $\omega_2$ are both exited the molecule acquires a purely vibrational angular momentum $l_{\text{vib}}$ so that in the vibrational state in which $l_{\text{vib}}$ is acting, the total angular momentum should be quantized as

$$l = |l_{\text{vib}}|, |l_{\text{vib}}| + 1, \ldots$$

in accordance with observed spectra. For a more accurate description is then necessary to consider anharmonicity and further rotovibrational interactions.
Now I come to the general analysis of the $XY_2$ molecule. Chosen the $xyz$ frame with the $z$ axis coinciding with the molecular axis, the orientation of the molecule does not depend on the $\gamma$ angle and the rotational configuration space reduces from $SO(3)$ to the sphere $S^2$. The Euler angles $\alpha, \beta$ coincide then with the standard $\phi, \theta$ spherical angles. The investigation of the $XY_2$ molecule is therefore reduced to the study of the immersion of the sphere $S^2$ in the six-dimensional euclidean space $R^6$. The rigid body metric on $S^2$ is given by

$$g_{\mu\nu} = \begin{pmatrix} I \sin^2 \beta & 0 \\ 0 & I \end{pmatrix},$$

(20)

Denoted by $\xi_1, \xi_{2a}, \xi_{2b}, \xi_3$ the normal vibrational coordinates, the only non-vanishing components of second fundamental form an normal fundamental form are

$$\alpha_1^{\mu\nu} = \begin{pmatrix} -\sqrt{I} \sin^2 \beta & 0 \\ 0 & -\sqrt{I} \end{pmatrix}$$

(21)

and

$$A_2^{\mu2b} = (\cos \beta, 0),$$
$$A_2^{\mu3} = (\sin \beta, 0),$$
$$A_2^{2b3} = (0, 1).$$

(22)

These quantities characterize the rotovibrational dynamics of the molecule completely [21]. For what concern the gauge field (11) only the term $A_2^{2a2b}$ is relevant. The effective rotational dynamics is described by Hamiltonian (10) with metric (20) and $A_2^{ij}$ given by (22). The motion on $S^2$ results then equivalent to that of a charged particle in a background magnetic-monopole field [8, 22]. Chosen the eigenvalues basis of $H^{(0)}$ is such a way that also $L_2a2b$ is diagonal, the monopole charge is proportional to the angular momentum of the degenerate oscillator $\langle L_2a2b \rangle$, that is to the vibrational angular momentum $l_{vib}$. $l_{vib}$ is always an integer. To discuss the motion in the monopole background it is convenient to introduce the angular momentum operators

$$\tilde{L}_1 = i(\cos \alpha \cot \beta \partial_\alpha + \sin \alpha \partial_\beta) + l_{vib} \frac{\cos \alpha}{\sin \beta},$$
$$\tilde{L}_2 = i(\sin \alpha \cot \beta \partial_\alpha - \cos \alpha \partial_\beta) + l_{vib} \frac{\sin \alpha}{\sin \beta},$$
$$\tilde{L}_3 = -i \partial_\alpha,$$

(23)
which close in the $SU(2)$ algebra. Then the rotational Hamiltonian (10) coincides, up to the $\bar{Q}$ potential, with that of a spherical top

$$\mathcal{H}^{(n_1,n_2,n_3)}_{\text{rot}} = \frac{\hbar^2}{2I} (\hat{L}^2 - l_{\text{vib}}^2),$$

(24)

the only effect of the monopole being that of making the rotational quantum number $l$ to take the values $l = [l_{\text{vib}}], [l_{\text{vib}}] + 1, \ldots$ [8, 22]. The monopole gauge field induced by the reduction of the motion from $R^6$ to $S^2$ takes therefore into account the absence of the first $[l_{\text{vib}}]$ values of the rotational quantum number $l$. This phenomenon is very close to that discovered by J. Moody, A. Shpere and F. Wilczek in the geometric phase analysis of diatoms [10].

To complete the analysis of the $XY_2$ spectrum at this order, cubic and quartic terms of the Born-Oppenheimer potential as well as the quantum potential $\bar{Q}$ have also to be taken into account. As well known anharmonicity contributes to the spectrum the correction

$$\Delta = 2\pi \hbar c \left( \sum_{p < q = 1}^3 x_{pq} (n_p + d_p/2)(n_q + d_q/2) + y l^2 \right)$$

(25)

(recall $d_1 = d_2 = 1, d_3 = 2$). Let us therefore concentrate on the potential $\bar{Q}$. Considered the explicit expression of the metric (20) and of the normal fundamental form (22) a straightforward computation produces

$$\bar{Q} = \frac{1}{2I} (\langle L_{2a3}^2 \rangle + \langle L_{3a3}^2 \rangle),$$

(26)

where the angled brackets denote expectation values in states with the same energy. The matrix potential (23) does not depend on rotational coordinates and results to be diagonal in every $H^{(0)}$'s eigenvalues basis. It contributes to the spectrum the correction

$$\Delta \bar{Q} = \frac{\hbar^2}{2I} \left( \frac{\omega_2}{\omega_3} + \frac{\omega_3}{\omega_2} \right)(n_2 + 1)(n_3 + 1/2)$$

(27)

As an example for the $CO_2$ molecule $x_{23} \simeq -11 \text{ cm}^{-1}$ whereas the coefficient $\hbar(\omega_2/\omega_3 + \omega_3/\omega_2)/4I\pi c$ may be estimated as $\simeq 2 \text{ cm}^{-1}$. Corrections of this kind have been foreseen in Ref. [18]. The analysis of the rigidity constraint proposed in this paper shades light on their geometrical nature giving a very general and compact formula to compute them.
6 Monopoles and Symmetric Tops

The Coriolis interaction between vibrational and rotational degrees of freedom in a linear molecule are taken into account by a background monopole field and a quantum potential acting on the rotational configuration space, the sphere $S^2$. In this and in the next section I consider the case in which the whole group $SO(3)$ is involved in the rotational dynamics, investigating the geometrical nature of Coriolis interactions in a symmetric top and a spherical top molecule. The problem requires the analysis of the embedding of $SO(3)$ in an appropriate $n$-dimensional euclidean space.

The simpler example of a symmetric top having degenerate frequencies is the equilateral $X_3$ molecule. Chosen the frame xyz with the molecule in the xy plane and denoted by $2I$ the momentum of inertia relative to the z axis, the rigid body metric on $SO(3)$ reads

$$g_{\mu\nu} = \begin{pmatrix} I(1 + \cos^2 \beta) & 0 & 2I \cos \beta \\ 0 & I & 0 \\ 2I \cos \beta & 0 & 2I \end{pmatrix}. \tag{28}$$

$X_3$ posses one simple, $\omega_1$, and one double, $\omega_2$, proper frequencies and I will denote by $\xi_1, \xi_{2a}, \xi_{2b}$ the corresponding vibrational coordinates. The second fundamental form and normal fundamental form of the embedding of $SO(3)$ in $R^6$ may easily be evaluated and result different from zero. For what concern the effective rotational motion only the normal fundamental form is relevant. Its nonvanishing component is given by

$$A^{2a2b}_\mu = (\cos \beta, 0, 0). \tag{29}$$

The rotational dynamics is described by Hamiltonian \([14]\) with $g_{\mu\nu}$ given by \((28)\) and $A^\mu_\nu$ by \((29)\). Chosen an eigenvalues basis of $H^{(0)}$ such that $L_{2a2b}$ is diagonal and denoted again with $l^{vib} = \langle L_{2a2b} \rangle$ the vibrational angular momentum, the motion on $SO(3)$ take place in presence of a background monopole-like field with charge $l^{vib}$. To discuss the $SO(3)$ dynamics in presence of the monopole is again possible to introduce adapted angular momen-
tum operators

\[ \tilde{L}_1 = i \left( \frac{\cos \gamma}{\sin \beta} \partial_\alpha - \sin \gamma \partial_\beta - \cot \beta \cos \gamma \partial_\gamma \right) - l^{vib} \cot \beta \cos \gamma, \]

\[ \tilde{L}_2 = i \left( \frac{\sin \gamma}{\sin \beta} \partial_\alpha + \cos \gamma \partial_\beta - \cot \beta \sin \gamma \partial_\gamma \right) - l^{vib} \cot \beta \sin \gamma, \]

\[ \tilde{L}_3 = -i \partial_\gamma - l^{vib}, \]

which close in the SU(2) algebra. Hamiltonian (10) for the \( X_3 \) molecule takes then the standard form

\[ H_{rot}^{(n_1, n_2)} = \frac{\hbar^2}{2I} (\tilde{L}_1^2 + \tilde{L}_2^2) + \frac{\hbar^2}{4I} (\tilde{L}_3 + l^{vib})^2. \]

introduced in Ref.[7] to take account of Coriolis coupling. The monopole field induced by the rigidity constraint in the effective rotational hamiltonian is therefore responsible for Coriolis interactions between vibrational and rotational degrees of freedom. The quantum potential (12) does not play any role in the description of the spectrum being identically zero.

7 Non-Abelian Monopoles and Spherical Tops

If a molecule has the symmetry of one of the cubical groups its proper frequencies may be triply degenerate and the gauge field appearing in the effective rotational Hamiltonian non-abelian. This is the case of spherical top molecules. The simpler example of physical interest is the tetrahedral \( XY_4 \) molecule. It possesses one simple, \( \omega_1 \), one double, \( \omega_2 \), and two triple, \( \omega_3, \omega_4 \), proper frequencies [18]. For sake of clearness I will however consider the simpler example of a tetrahedral \( Y_4 \) molecule in which the effect I want to point out already appears. \( Y_4 \) may be thought as an \( XY_4 \) in which the second triple degenerate normal mode may be neglected. Chosen the xyz frame fixed in the equilibrium configuration of the molecule in such a way that the four atoms lie in the positions \( \left( \frac{1}{\sqrt{8}}, \frac{1}{\sqrt{8}}, \frac{1}{\sqrt{8}} \right), \left( -\frac{1}{\sqrt{8}}, -\frac{1}{\sqrt{8}}, \frac{1}{\sqrt{8}} \right), \left( \frac{1}{\sqrt{8}}, -\frac{1}{\sqrt{8}}, -\frac{1}{\sqrt{8}} \right), \left( -\frac{1}{\sqrt{8}}, \frac{1}{\sqrt{8}}, -\frac{1}{\sqrt{8}} \right) \).
\((\frac{1}{\sqrt{8}}, \frac{1}{\sqrt{8}}, -\frac{1}{\sqrt{8}})\) and denoted by \(I\) the momentum of inertia relative to the axis x, y and z, the rigid body metric on \(SO(3)\) reads

\[
g_{\mu \nu} = \begin{pmatrix} I & 0 & I \cos \beta \\ 0 & I & 0 \\ I \cos \beta & 0 & I \end{pmatrix}.
\] (32)

The second fundamental form and normal fundamental form of the embedding of \(SO(3)\) in \(R^9\) may also be easily evaluated. Denoting as before with \(\xi_1, \xi_2, \xi_3, \xi_3, \xi_3, \xi_3\) the normal coordinates, the nonvanishing components of the normal fundamental form reads

\[
A_{\mu}^{2a3a} = \left( \frac{1 + \sqrt{3}}{2\sqrt{2}} \sin \beta \sin \gamma, -\frac{1 + \sqrt{3}}{2\sqrt{2}} \cos \gamma, 0 \right),
\]

\[
A_{\mu}^{2a3b} = \left( \frac{1 - \sqrt{3}}{2\sqrt{2}} \sin \beta \cos \gamma, \frac{1 - \sqrt{3}}{2\sqrt{2}} \sin \gamma, 0 \right),
\]

\[
A_{\mu}^{2a3c} = \left( \frac{1}{\sqrt{2}} \cos \beta, 0, \frac{1}{\sqrt{2}} \right),
\]

\[
A_{\mu}^{2b3a} = \left( \frac{1 - \sqrt{3}}{2\sqrt{2}} \sin \beta \sin \gamma, \frac{1 - \sqrt{3}}{2\sqrt{2}} \cos \gamma, 0 \right),
\]

\[
A_{\mu}^{2b3b} = \left( \frac{1 + \sqrt{3}}{2\sqrt{2}} \sin \beta \cos \gamma, \frac{1 + \sqrt{3}}{2\sqrt{2}} \sin \gamma, 0 \right),
\]

\[
A_{\mu}^{2b3c} = \left( -\frac{1}{\sqrt{2}} \cos \beta, 0, -\frac{1}{\sqrt{2}} \right)
\]

and

\[
A_{\mu}^{3a3a} = \left( \frac{1}{2} \cos \beta, 0, -\frac{1}{2} \right),
\]

\[
A_{\mu}^{3a3b} = \left( -\frac{1}{2} \sin \beta \sin \gamma, -\frac{1}{2} \cos \gamma, 0 \right),
\]

\[
A_{\mu}^{3c3a} = \left( \frac{1}{2} \sin \beta \cos \gamma, -\frac{1}{2} \sin \gamma, 0 \right).
\]

The effective rotational motion is again described by Hamiltonian (10) with \(g_{\mu \nu}\) the spherical top metric (32) and \(A_{\mu}^{ij}\) given by (33). The vibrational angular momentum is not in general diagonalizable. Nevertheless in every vibrational state labelled by the quantum numbers \(n_1, n_2\) and \(n_3\), the matrices
\[ L^\text{vib}_1 = \langle L_{3a3a} \rangle / \hbar, \quad L^\text{vib}_2 = \langle L_{3b3b} \rangle / \hbar \quad \text{and} \quad L^\text{vib}_3 = \langle L_{3a3b} \rangle / \hbar \]
form a \( n_2(n_2 + 1)(n_3 + 1)(n_3 + 2) / 4 \)-dimensional representation of the Lie algebra of \( SO(3) \) so that \( A_\mu \) is an \( SO(3) \) gauge potential presenting the characteristic of a non-abelian monopole. Stated in other words we are facing the dynamical problem of the motion on the group \( SO(3) \) in presence of a non-abelian monopole whose gauge group is again \( SO(3) \). Once more we address the solution by considering appropriate angular momentum operators which close in the \( SU(2) \) algebra

\[
\begin{align*}
\tilde{L}_1 &= i \left( \frac{\cos \gamma}{\sin \beta} \partial_\alpha - \frac{1}{\sin \gamma} \partial_\beta - \cot \beta \cos \gamma \partial_\gamma \right), \\
\tilde{L}_2 &= i \left( \frac{\sin \gamma}{\sin \beta} \partial_\alpha + \cos \gamma \partial_\beta - \cot \beta \sin \gamma \partial_\gamma \right), \\
\tilde{L}_3 &= -i \partial_\gamma.
\end{align*}
\]

(34)

Introduced the vector matrix \( L^\text{vib} = (L^\text{vib}_1, L^\text{vib}_2, L^\text{vib}_3) \) and denoting by \( 1 \) the \( n_2(n_2 + 1)(n_3 + 1)(n_3 + 2) / 4 \)-dimensional identity matrix, Hamiltonian (10) for the \( Y_4 \) molecule assume the standard form \[7\]

\[
H_{\text{rot}}^{(n_1, n_2, n_3)} = \frac{\hbar^2}{2I} \left( 1 \tilde{L} - \frac{1}{2} L^\text{vib} \right)^2, \tag{35}
\]

up to the \( \bar{Q} \) potential. In a spherical top molecule Coriolis interactions are therefore described by means of a non-abelian monopole gauge field induced in the effective rotational dynamics by the rigidity constraint.

The quantum potential \( \bar{Q} \) plays also an important role in the description of rotovibrational interactions. The use of the explicit form of the metric (12) and of the normal fundamental form (33) allows to rewrite the general formula (12) as

\[
Q = \frac{\hbar^2}{8I} \left( \langle L^2_{2a3a} + L^2_{2a3b} + L^2_{2b3a} + L^2_{2b3b} + L^2_{2b3c} \rangle + \right.
\left. + \sqrt{3} \langle L^2_{2a3a} - L^2_{2b3a} \rangle - \sqrt{3} \langle L^2_{2a3b} - L^2_{2b3b} \rangle + \right.
\left. + \langle L_{2a3a} L_{2b3a} + L_{2b3a} L_{2a3a} \rangle + \langle L_{2a3b} L_{2b3b} + L_{2b3b} L_{2a3b} \rangle + \right.
\left. - 2 \langle L_{2a3c} L_{2b3c} + L_{2b3c} L_{2a3c} \rangle \right).
\]

19
To evaluate the expectation values is convenient to rewrite vibrational angular momentum operators in terms of destruction and creation operators

\[
\begin{cases}
    a_i = \sqrt{\frac{\hbar}{2\Omega}}(\xi_i + \frac{1}{\omega_i}\partial_{\xi_i}) \\
    a_i^\dagger = \sqrt{\frac{\hbar}{2\Omega}}(\xi_i - \frac{1}{\omega_i}\partial_{\xi_i})
\end{cases}
\]  

(36)

for \(i = 2a, 2b, 3a, 3b, 3c\). Computation conduces then to the expression

\[
\hat{Q} = \frac{\hbar^2}{8I} \left(\frac{\omega_3}{\omega_2} + \frac{\omega_2}{\omega_3}\right) \times \\
\left(2(a_{2a}^\dagger a_{2a} + a_{2b}^\dagger a_{2b} + 1)(a_{3a}^\dagger a_{3a} + a_{3b}^\dagger a_{3b} + 1) + \right.
\]

\[
+ (a_{2a}^\dagger a_{2b} + a_{2b}^\dagger a_{2a})(a_{3a}^\dagger a_{3a} + a_{3b}^\dagger a_{3b} - 2a_{3c}^\dagger a_{3c}) + \\
\left. \right|_{2} \right) \\
\sqrt{3}(a_{2a}^\dagger a_{2a} - a_{2b}^\dagger a_{2b})(a_{3a}^\dagger a_{3a} - a_{3b}^\dagger a_{3b})
\]  

(37)

which is not diagonal in the standard basis of \(H^{(0)}\). Nevertheless \(\left[H^{(0)}, \hat{Q}\right] = 0\) so that the diagonalization of \(\hat{Q}\) is possible. We achieve this aim by performing a rigid gauge transformation in the \(\xi_{2a}, \xi_{2b}\) subspace in correspondence of every \(n_{3a}, n_{3b}, n_{3c}\), \(n_i\) denotes, of course, the quantum number created by \(a_i^\dagger\); \(n_2 = n_{2a} + n_{2b}, n_3 = n_{3a} + n_{3b} + n_{3c}\), that is by rotating creation-destruction operators by

\[
\begin{cases}
    a_+ = \cos \psi a_{2a} + \sin \psi a_{2b} \\
    a_- = -\sin \psi a_{2a} + \cos \psi a_{2b}
\end{cases}
\]  

(38)

where

\[
\cos \psi = \frac{1}{\sqrt{2}} + \frac{\sqrt{3}}{4\sqrt{n_{3a}^2 + 2n_{3a}^2 + n_{3c}^2 - n_{3a}n_{3b} - n_{3b}n_{3c} - n_{3c}n_{3a}}}
\]

\[
\sin \psi = \frac{1}{\sqrt{2}} - \frac{\sqrt{3}}{4\sqrt{n_{3a}^2 + 2n_{3a}^2 + n_{3c}^2 - n_{3a}n_{3b} - n_{3b}n_{3c} - n_{3c}n_{3a}}}
\]

Rewriting \(\hat{Q}\) in terms of \(a_+, a_+^\dagger, a_-, a_-^\dagger\) and denoting by \(n_+, n_-\) \((n_2 = n_+ + n_-)\) the corresponding quantum numbers, we obtain the correction to the spectrum

\[
\Delta \hat{Q} = \frac{\hbar^2}{4I} \left(\frac{\omega_3}{\omega_2} + \frac{\omega_2}{\omega_3}\right) \left[ (n_2 + 1)(n_3 + 3/2) + \\
+ 2(n_+ - n_-)\sqrt{n_{3a}^2 + 2n_{3a}^2 + n_{3c}^2 - n_{3a}n_{3b} - n_{3b}n_{3c} - n_{3c}n_{3a}} \right]
\]  

(39)
$Q$ contributes therefore in removing the vibrational degeneracy together with anharmonic terms of the Born-Oppenheimer potential.

As for the $XY_2$ and the $X_3$ molecules, gauge fields and quantum potential induced by the reduction of the quantum dynamics from $R^3$ to $SO(3)$ take naturally into account rotovibrational interactions giving a general and simple way to compute them.

8 Concluding Remarks

In this paper I discussed the constrained motion of a quantomechanical system by explicitly considering the mechanism realizing the constraint. This gives rise to a very rich dynamical structure unrecoverable with the standard techniques. I focused my attention on the first order term of the perturbative expansion (6), showing how gauge fields and quantum potentials induced in the effective dynamics are responsible for leading order rotovibrational interactions in polyatomic molecules. The main results of the paper are

— The interpretation of the standard Hamiltonians (24), (31) and (35), describing Coriolis interactions in linear, symmetric top and spherical top molecules, in terms of the general Hamiltonian (10). This illustrates that the gauge field (11) is relevant in the description of constrained systems, giving an explicit realization in nature of abelian and non-abelian monopole fields.

— The very general and compact expression (12) to compute corrections to molecular spectra given by the other leading order rotovibrational interactions, such as (27) for the $XY_2$ molecule and (39) for the $Y_4$ molecule.

— A complete geometrical characterization of molecular rotovibrational dynamics, showing how the intrinsic and extrinsic geometrical properties of the embedding of the rotational group $SO(3)$ in the configuration space $R^n$, together with the Born-Oppenheimer potential, completely determine the rotovibrational spectrum of a polyatomic molecule.
It is possible to demonstrate that the whole perturbative expansion (6) is completely characterized by $g_{\mu\nu}$, $\alpha^i_{\mu\nu}$ and $A^{ij}_{\mu}$ giving the explicit expression of the arbitrary order term [24]. The method is therefore suitable for a complete perturbative analysis of the spectra of rigid molecules. I want to point out that this does not constitute an alternative to the standard techniques [20], but, rather, an improvement in the light of the general considerations of section 3 and Refs. [1, 6, 21]. Besides the problem of taking into account finer corrections of rigid molecular spectra by considering further terms of expansion (6), several other questions remain open. It is possible, for example, to correlate the form of the monopole gauge field appearing in the effective rotational dynamics to the symmetry of the molecule, is such a way that effective Hamiltonians for more complex molecules may be written automatically? It is possible, by resumming part of expansion (6), to take into account non-rigidity effects in molecular spectra? More in general it would be interesting to investigate the relation between constrained quantum mechanics and geometric phases.

To conclude I want to point out the very important fact that the perturbative expansion (6) for molecular systems writes naturally in terms of modified angular momentum operators and creation/destruction operators corresponding to normal modes, so that the evaluation of molecular spectra and eigenfunctions may be performed completely by means of algebraic manipulations [23].

Acknowledgments

I wish to warmly thank C. Destri and E. Onofri for useful discussions.

References

[1] P. Maraner and C. Destri, Mod. Phys. Lett. A8, 9 861 (1993)

[2] H. Jensen and H. Koppe, Ann. of Phys. 63, 586 (1971)

[3] R. A. Marcus, J. Chem. Phys. 45, 4493 (1966); M. Kugler and S. Shtrikman, Phys. Rev. D37, 934 (1988); R. C. T. da Costa, Phys. Rev.
[4] S. Takagi and T. Tanzawa, *Prog. Theo. Phys.* 87, 561 (1992)

[5] H. P. Berg, *Lett. Math. Phys.* 6, 183 (1982); J. Tolar, in *Lectures Notes in Physics* 313, ed. H. D. Doever J. D. Henning and T. D. Raev (Springer-Verlag, 1988); T. Homma, T. Inamoto and T. Miyazaki, *Phys. Rev.* D42, 2049 (1990); N. Ogawa, K. Fujii and A. Kobushukin, *Prog. Theo. Phys.* 83, 894 (1990); N. Ogawa, K. Fujii, N. Chepilko and A. Kobushukin, *Prog. Theo. Phys.* 85, 894 (1991); N. Ogawa, *Prog. Theo. Phys.* 87, 513 (1992); C. Destri, P. Maraner and E. Onofri, *Nuovo Cimento* A107, 237 (1994)

[6] K. Fujii and N. Ogawa, *Prog. Theo. Phys.* 89, 575 (1993)

[7] E. Teller, *Hand- und Jahrbuch d. Chem. Physik* 9, 125 (1934); M. Johnston and D. M. Dennison, *Phys. Rev.* 48, 868 (1935)

[8] P. A. M. Dirac, *Proc. Roy. Soc.* A133, 60 (1931)

[9] C. N. Yang and R. L. Mills, *Phys. Rev.* 96, 191 (1954)

[10] J. Moody, A. Shpere and F. Wilczek, *Phys. Rev. Lett.* 56, 9199 (1986)

[11] For a review on Geometric Phases in Molecular Physics see C. A. Mead, *Rev. Mod. Phys.* 64, 1 (1992); A. Bohm, B. Kendrik and M. E. Loewe, *Int. Jou. Q. Chem.* 41, 53 (1992)

[12] M. V. Berry, *Proc. Roy. Soc.* A392, 45 (1984); B. Simon, *Phys. Rev. Lett.* 51, 2167 (1983); F. Wilczek and A. Zee, *Phys. Rev. Lett.* 52, 2111 (1984)

[13] For a review see *The Quantum Hall Effect*, ed. R. E. Prange and S. M. Girvin (Springer-Verlag, 1989)

[14] See, for example, M. Spivak, *Differential Geometry* Vol. IV (Publich or Perich Inc., 1975)

[15] J. S. Dowker, in *Functional Integration and its Application*, A. M. Arthurs ed., (Clarendon Oxford, 1975)
[16] M. Ikegami and Y. Nogaka, *Prog. Theo. Phys. Supp.* **106**, 235 (1991)

[17] For a review see *Geometric Phases in Physics*, ed. A. Shpere, F. Wilczek (World Scientific, Singapore, 1989)

[18] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules and II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold Company, 1945)

[19] See, for example, R. S. Berry in *Quantum Dynamics of Molecules* ed. R. G. Woolley (Plenum, New York, 1980)

[20] H. H. Nilesen, *Rev. Mod. Phys.* **32**, 90 (1951)

[21] P. Maraner “A Complete Perturbative Expansion for Constrained Quantum Dynamics” Parma Preprint, in preparation

[22] T. T. Wu, C. N. Yang, *Phys. Rev.* **D12**, 3845 (1975); T. T. Wu, C. N. Yang, *Nuc. Phys.* **B107**, 365 (1976); C. N. Yang, in *Understanding the Fundamental Constituents of Matter*, ed. A. Zichichi (Plenum, New York, 1978)

[23] F. Iachello, *Chem. Phys. Lett.* **78**, 581 (1981); F. Iachello and R. D. Levine, *Jou. Chem. Phys.* **77**, 3046 (1982); O. S. van Roosmalen, F. Iachello, D. R. Levine and A. E. L. Dieperink, *Jou. Chem. Phys.* **79**, 2515 (1983); F. Iachello, A. Leviatan and A. Mengoni, *Jou. Chem. Phys.* **95**, 1449 (1991); F. Iachello, *Int. Jou. Qua. Chem.* **41**, 77 (1992)