JJ

Rydberg states of atoms and molecules.
Basic group theoretical and topological analysis.

L. MICHEL

B. ZHILINSKII

Swg747

Institut des Hautes Etudes Scientifiques
35, route de Chartres
91440 – Bures-sur-Yvette (France)

Juillet 1997

IHES/P/97/54

Rydberg states of atoms and molecules. Basic group theoretical and topological analysis.

L. Michel*, B. Zhilinskii⁺

*IHES, F91440 Bures-sur-Yvette, FRANCE

⁺ Université du Littoral, F59379 Dunkerque, FRANCE

Rydberg states of atoms and molecules are studied within the qualitative approach based primarily on topological and group theoretical analysis. The correspondence between classical and quantum mechanics is explored to apply the results of qualitative (topological) approach to classical mechanics developed by Poincaré, Lyapounov, Smale to quantum problems. The study of the action of the symmetry group of the problem considered on the classical phase space enables us to predict qualitative features of the energy level patterns for quantum Rydberg operators.

Contents

I	Introduction	2
II	Basic Concepts	4
A	Group actions and their strata	4
1	Examples.	5
B	G -invariant functions. Their extrema	7
1	Rings of G -invariant functions	8
2	Extrema of G invariant functions	11
C	Morse theory.	12
D	Qualitative analysis for classical limits.	14
1	Purely rotational Hamiltonian	16
2	Vibrational polyads	17
3	Dynamical symmetry of Rydberg states.	17
III	Groups and their actions appropriate for the Rydberg problem	18
A	Structure of $O(4)$	18
B	The adjoint representation of $O(4)$; induced action on $\Sigma = S_2 \times S_2$	19
1	Extension of $O(4)$ by including the time reversal	20
2	The action of $O(4) \wedge T$ on the vector space V of the adjoint representation and on the phase space Σ	20
C	Action of $O(3)$, $SO(3)$, $O(3) \wedge T$, $SO(3) \wedge T$, and $SO(3) \wedge T_s$ on Σ ; their strata, orbits and invariants	21
D	Invariants of the one dimensional Lie subgroups of $O(3)$ acting on Σ	22
E	One dimensional Lie subgroups of $O(3) \wedge T$ and their invariants	24

F	Orbits, strata and orbit spaces of one dimensional Lie subgroups of $O(3)$ acting on Σ	26
G	Invariants of finite subgroups of $O(3)$ acting on Σ	28
H	Orbits, strata and orbit spaces of finite subgroups of $O(3)$ acting on Σ	29
I	Orbits, strata, and orbit spaces for T -dependent subgroups of $O(3) \wedge T$	29

IV	Construction and analysis of Rydberg Hamiltonians.	32
A	Effective Hamiltonians	32
B	Qualitative description of effective Hamiltonians invariant with respect to continuous subgroups of $O(3)$	34
1	$O(3)$ invariant Hamiltonian	34
2	C_∞ invariant Hamiltonian	34
3	$C_{\infty v}$ invariant Hamiltonian	35
4	$C_{\infty h}$ invariant Hamiltonian	36
5	D_∞ invariant Hamiltonian	36
6	$D_{\infty h}$ invariant Hamiltonian	36
C	Qualitative description of effective Hamiltonians invariant with respect to finite subgroups of $O(3)$	36
V	Manifestation of qualitative effects in physical systems. Hydrogen atom in magnetic and electric field.	38
A	Different field configurations and their symmetry.	39
B	Quadratic Zeeman effect in hydrogen atom	40
C	Hydrogen atom in parallel electric and magnetic fields	41
D	Hydrogen atom in orthogonal electric and magnetic fields	44
E	Where to look for bifurcations?	47
VI	Conclusions and perspectives	47
	APPENDIXES	49
A	Geometrical representation	49
1	$O(3)$ or $SO(3)$ invariant Hamiltonian	49
2	C_∞ invariant Hamiltonian	50
3	$C_{\infty v}$ invariant Hamiltonian	51
4	$C_{\infty h}$ invariant Hamiltonian	52
5	D_∞ invariant Hamiltonian	53
6	$D_{\infty h}$ invariant Hamiltonian	54

B	Molien functions for point group invariants.	55
1	C_1 group	55
2	C_2 point group	55
3	C_i point group	56
4	C_s point group	56
5	C_{2v} point group	56
6	D_{3h} group	57
7	T_d point group	59
C	Strata and orbits for point groups.	60
D	Qualitative description of effective Hamiltonians. Analysis based on equivariant Morse-Bott theory	61
1	Compilation of Bott and Kirwan about the construction of equivariant homology.	61
2	$SO(3)$ continuous subgroup.	64
3	C_∞ continuous subgroup.	64
E	Physical examples of systems and phenomena with continous subgroups of $O(3) \wedge T$ as symmetry groups	65
1	One dimensional Lie subgroups of $O(3) \wedge T$	65
2	Three dimensional Lie subgroups of $O(3) \wedge T$	66

I. INTRODUCTION

This paper is the first one of a planned series of papers (with different authors) on Rydberg states of atoms and molecules (Sadovskii, Zhilinskii, and Michel, 1996; Sadovskii and Zhilinskii, 1997). Those are very slightly bound quantum states of an electron and a positively charged ion. In the approximation one can neglect the excitations of the ionic core and all spin effects, the spectrum of states has a structure typical of that of the hydrogen atom: grouping in multiplets of n^2 states for large principal quantum number n . Below we will explain that we shall restrict ourselves to the analysis of the internal structure of these large Rydberg multiplets when their splitting is small in some sense.

The experimental study of Rydberg states is a very active field of physics (Aymar, 1984; Stebbing, 1983). There are many works on Rydberg atoms isolated or in different configurations of magnetic and electric fields (Beims, 1993; Boris, 1993; Cacciani, 1988, 1989, 1992; Fabre, 1977, 1984; Flöthmann, 1994; Frey, 1996; Fujii, 1994; Hulet, 1983; Jacobson, 1996; Jones, 1996; König, 1988; Lahaye, 1989; Raithel, 1991, 1993, 1995; Rinneberg, 1985; Rothery, 1995; Seipp, 1996; Veldt, 1993; Zimmerman, 1979). The study of Rydberg molecules is beginning (Bordas, 1985; Bordas and Helm, 1991, 1992; Bordas, Lembo, and Helm, 1991; Broyer, 1986; Dabrowski, 1992, 1994; Davies, 1990; Dietrich, 1996; Dodhy, 1988; Harris, 1993; Helm, 1986, 1988; Herzberg,

1987; Herzberg and Jungen, 1972; Hiskes, 1996; Jungen, 1988, 1989, 1990; Ketterle, 1989; Labastie, 1984; Lembo, 1989, 1990; Mayer, 1995; Merkt, 1995, 1996; Schwarz, 1988; Sturru, 1988; Weber, 1996).

Theoretical studies also exist for each type of experiments (Aymar, 1996; Bander, 1966; Bixon, 1996; Braun, 1993; Braun and Solov'ev, 1984; Chiu, 1986; Clark, 1996; Delande, 1986, 1988, 1991, 1994; Delos, 1983; Englefield, 1972; Fano, 1992; Farrelly, 1994; Farrelly and Krantzman, 1991; Farrelly and Milligan, 1992; Farrelly, Uzer, *et al.*, 1992; Friedrich, 1989; Gourlay, 1993; Greene, 1985; Hasegawa, 1989; Herrick, 1982; Howard, 1995; Huppner, 1996; Iken, 1994; Kalinski, 1996a, 1996b; Kazanskii, 1989, 1990; Kelleher, 1987; King, 1979; Kuwata, 1990; Laughlin, 1995; Lombardi, 1988, 1993; Mao, 1992; Pan, 1988; Rabani, 1996; Rau, 1990; Remacle, 1996a, 1996b; Robnik, 1985; Solov'ev, 1981, 1982, 1986; Stephens, 1995; Tanner, 1996; Thoss, 1995; Uzer, 1990; Zakrzewski, 1995).

It is time to establish some general physical laws applying to the Rydberg multiplets. They can be obtained by a general qualitative analysis of the relevant problems based on general methods that we shall explain in this initial paper of the series and illustrate by few simple examples. Further applications to atomic and molecular problems will be treated separately (Sadovskii, Zhilinskii, and Michel, 1996; Sadovskii and Zhilinskii, 1997).

Two features of Rydberg physics make attractive a general approach:

First, when the external fields are small enough or vanish, each Rydberg multiplet is labeled by the value n of the principal quantum number and the splitting inside the each multiplet is small compared to the splitting between them. The dynamical system which describes the internal structure of an individual n multiplet has two degrees of freedom. For large n , the set of n^2 quantum levels is sufficiently large to be well studied by classical analysis, as a Hamiltonian dynamical system defined on a four dimensional phase space with nontrivial topology and symmetry that we shall soon precise (see IID).

Second, the isolated hydrogen atom has a large dynamical symmetry: that of the orthogonal group $O(4)$ and time reversal. As we shall recall, that is an exact symmetry for the quantum mechanical study, in the non relativistic approximation, of an electron in the static Coulomb potential of a point-like nucleus; then the energy of bound states depends only on the principal quantum number n ; that exceptional energy degeneracy between the states of different orbital momenta of value ℓ , $0 \leq \ell \leq n-1$ contains $\sum_{\ell} (2\ell+1) = n^2$ states whose state vectors form the space of an irreducible linear representation of $O(4)$. For atomic or molecular ions the $O(4)$ dynamical symmetry is only an initial approximation for the Rydberg states, which becomes exact at the asymptotic limit $n \rightarrow \infty$ when there are no external fields. Their geometric symmetry is that of the positive ion: it is at most $O(3)$ (case of the isolated hydrogenoid atom) and it is a finite subgroup of $O(3)$ in the case of non

TABLE I. Physical examples of the geometric invariance subgroups of Rydberg atoms and molecules.

$O(3)$	Rydberg atoms with the closed shell core
$C_{\infty v}$	Rydberg atoms under the presence of a weak electric field.
Heteronuclear diatomic Rydberg molecule AB	
$C_{\infty h}$	Rydberg atoms under the presence of a weak magnetic field
C_{∞}	Rydberg atoms under the presence of parallel magnetic and electric fields
$D_{\infty h}$	Homonuclear diatomic Rydberg molecules A_2
Point group	Polyatomic Rydberg molecules with the point group symmetry G
G	H_3 (D_{3h}), NH_4 (T_d), ...

aligned molecules. Several important physical examples of geometric symmetry are listed in the Table I. Further extension of geometric invariance groups to higher symmetry groups including time reversal operation will be discussed as well (Section IIII).

As it is well known, the quantum mechanical study of the hydrogen atom, in the non relativistic approximation, was first made by Pauli (1926) just before the appearance of the Shrödinger equation. In a convenient unity system, the Hamiltonian for a hydrogen atom can be written:

$$H = \frac{1}{2\mu} p^2 - \frac{1}{r}; \quad E_n = -\frac{1}{2n^2}. \quad (1)$$

Due to the specific Coulomb interaction there are two vector integrals of motion: $\mathbf{J}$ - the angular momentum vector, and $\mathbf{X}$ - the Laplace-Runge-Lenz vector,

$$\mathbf{X} = \mathbf{p} \times \mathbf{J} - \mathbf{r}r^{-1}. \quad (2)$$

In other words the Hamiltonian operator H commutes with the vector operators $\mathbf{J}$ and $\mathbf{X}$ and all their functions.

After the energy dependent scaled transformation

$$\mathbf{K} = \mathbf{X}(-2E_n)^{-1/2} = \mathbf{X}n, \quad (3)$$

it was shown by Hulthen (1933) and Fock (1936), that $\mathbf{J}$ and $\mathbf{K}$ form Lie algebra with defining commutation relations

$$[J_\alpha, J_\beta] = i\varepsilon_{\alpha\beta\gamma} J_\gamma, \quad (4a)$$

$$[J_\alpha, K_\beta] = i\varepsilon_{\alpha\beta\gamma} K_\gamma, \quad (4b)$$

$$[K_\alpha, K_\beta] = i\varepsilon_{\alpha\beta\gamma} J_\gamma, \quad (4c)$$

We shall show in III A that this Lie algebra is the one of the group $O(4)$ or $SO(4)$ (or several other groups). In the hydrogen atom the operators $\mathbf{J}, \mathbf{K}$ satisfy moreover the two important relations

$$\mathbf{J} \cdot \mathbf{K} = \mathbf{K} \cdot \mathbf{J} = 0; \quad (5a)$$

$$\mathbf{J}^2 + \mathbf{K}^2 = n^2 - 1. \quad (5b)$$

which give the value of the two $SO(4)$ Casimir operators for the Hilbert space of vector states with the energy

E_n . Instead of $\mathbf{J}$ and $\mathbf{K}$ we can introduce the two linear combinations:

$$\mathbf{J}_1 = (\mathbf{J} + \mathbf{K})/2; \quad (6a)$$

$$\mathbf{J}_2 = (\mathbf{J} - \mathbf{K})/2. \quad (6b)$$

Using only the relations (4) one verifies that these operators satisfy:

$$[J_{k\alpha}, J_{k\beta}] = i\varepsilon_{\alpha\beta\gamma} J_{k\gamma}, \quad k = 1, 2; \quad (7a)$$

$$[J_{1\alpha}, J_{2\beta}] = 0. \quad (7b)$$

That shows that the Lie algebra of $SO(4)$ is isomorphic to the Lie algebra of the direct product $SU(2) \times SU(2)$ of two groups $SU(2)$. Therefore an irreducible representations of $SO(4)$ can be labeled by a pair (j_1, j_2) ; its dimension is $(2j_1 + 1)(2j_2 + 1)$. The relations (6) imply $\mathbf{J}_1^2 - \mathbf{J}_2^2 = \mathbf{J} \cdot \mathbf{K}$. Then (5a) is equivalent to

$$\mathbf{J}_1^2 = \mathbf{J}_2^2. \quad (8)$$

This last relation proves that the relevant $SO(4)$ irreducible representations for the Rydberg problems are of the form (j, j) with $n = 2j + 1$; hence its dimension is n^2 .

The richness of the Rydberg problem makes very interesting and powerful its “qualitative” study (Bandar, 1966; Boiteux, 1973, 1982; Byers Brown, 1966; Coulson, 1967; Cushman, 1997; Englefield, 1972; Guillemin, 1990; Iwai, 1981a, 1981b, 1986; McIntosh, 1970; Stiefel, 1971). For the convenience of the reader Section II recalls the many and fascinating basic tools needed for the general approach. We introduce the general approach by using different examples from molecular physics which are less complicated from the point of view of the mathematical technique and give to the reader the opportunity to get the unified qualitative approach developed recently for molecular rotation, vibration, and rovibration problems (Pavlichenkov, 1988; Sadovskii, 1988, 1993a, 1993b; Zhilinskii, 1989a, 1989b, 1996; Zhilinskii, Brodersen, and Madsen, 1993).

Section III will give a more thorough study of the symmetry we have to use. The main result of this section is the description of the symmetry group action on the phase space, construction of the rings of the polynomial invariant functions and the orbifolds for all cases of the continuous invariant symmetry groups of the Rydberg problem and for finite point symmetry groups. Section IV gives the construction and properties of phenomenological Rydberg Hamiltonians based on the integrity bases constructed in Section III. Section V will study some examples of qualitative effects. We restrict ourselves with the application of the technique developed to the problem of the hydrogen atom in external electric and magnetic fields. In spite of the fact that this problem seems to be well understood [see, for example, recent reviews by Friedrich and Wintgen (1989), Hasegawa, Robnik, and Wunner (1989), and Braun (1993)] it is still possible to find new features and to give different (and we

hope useful) interpretation of some qualitative modifications of the dynamical behavior. In particular, the simple geometrical description of the collapse phenomenon is given recently by Sadovskii, Zhilinskii, and Michel (1996). It is based on the orbifold construction introduced in this paper. The conclusion summarizes briefly further steps to apply the technique developed in this paper to a much wider class of molecular problems. The appendices give more details about the time-dependent symmetry groups and their physical realization, about geometrical representation of Rydberg orbifolds, explain more technical mathematical constructions like Molien functions or equivariant Morse-Bott approach, and collect some auxiliary tables needed for further application of the qualitative approach to molecular problems with finite point symmetry group.

II. BASIC CONCEPTS

This section recalls some important mathematical and physical concepts that we shall use for the qualitative analysis of Rydberg state problems. These basic notions are presented on a more general footing; we illustrate them all along the whole section with examples less complicated than the Rydberg problem. Subsection II A recalls what is the action of a group G on a manifold M and what are the corresponding strata. In subsection II B we explain how to describe the set of G -invariant functions on M with the help of invariant polynomials and how to use these polynomials to label orbits of the group action (we realize the construction of orbifold in invariant polynomial variables). In the same subsection we formulate some general statements concerning the localization of the extrema of G -invariant functions on M . In a given group action all invariant functions have in common some orbits of extrema; we call them *critical orbits*. Some conditions on the nature of the critical and of all other extrema are imposed by Morse theory (extended to manifolds of extrema by Bott) as explained in subsection II C. In subsection II D we explain the possibility of qualitative analysis of quantum problems through the topological study of corresponding classical limits. Both a local and a global study depend on the nature of the extrema of the invariant functions; these extrema correspond to stationary points (or G -orbits). At last the manifold corresponding to the classical limit of the Rydberg problem will be defined.

For more details on the contents of the first three subsections we refer to Atiyah and Bott (1982), Bott (1982), Dubrovin (1990), Jaric (1984), Kirwan (1988), Michel (1971, 1972, 1978, 1979, 1980), and Morse (1925); for subsection II D to Abraham (1978), Arnol'd (1981, 1988); Gilmore (1981), Pavlichenkov (1988), Poston (1978), Sadovskii and Delos (1996), Sadovskii and Zhilinskii (1988, 1993a, 1993b), and Zhilinskii (1989a, 1989b, 1996).

A. Group actions and their strata

Groups intervene in physics through their actions. **Definition: group action.** An action of a group G on a mathematical structure M is defined by a homomorphism $G \xrightarrow{\rho} \text{Aut } M$ into the group of automorphisms of M . We generally assume that $\ker \rho = 0$; in that case the action is called *effective*; otherwise we will indicate the kernel.

Next comes naturally the

Definition: equivalence of group actions. The two actions $G \xrightarrow{\rho_1} \text{Aut } M_1$ are equivalent if there exists an isomorphism: $M_1 \xrightarrow{\theta} M_2$ which is *equivariant*, i.e. which commute with the two actions:

$$\forall g \in G : \quad \theta \circ \rho_1(g) = \rho_2(g) \circ \theta. \quad (9)$$

When we consider a unique action of G on M we generally shorten the notation $\rho(g)(m)$, the transform of $m \in M$ by $g \in G$, into $g.m$.

When M is a n -dimensional orthogonal space, that we will usually denote by V_n (or, more generally, a Hilbert space), $\text{Aut } V_n$ is the orthogonal group $O(n)$ (correspondingly, the unitary group $U(n)$) and the action ρ defines an orthogonal (correspondingly, a unitary) linear representation of G on V_n . The usual equivalence of group representations is a particular case of the equivalence of group actions.

Definition: group orbit. The set of transforms of m , that we denote by $G \cdot m$, is the *orbit* of m .

An orbit may have a unique element! this is a "fixed point". More generally, to be on the same orbit is an equivalence relation for the elements of M . So M is a disjoint union of its orbits. The set of orbits is called the *orbit space* and we denote it by $M|G$.

An orthogonal linear representation of G on V defines implicitly an action on any manifold M , submanifold of V , which is a union of G -orbits.

Definition: stabilizer. The set $G_m = \{g \in G, g \cdot m = m\}$ of elements of G which leave m fixed, is the *stabilizer* of m ; it is a subgroup of G .

For a fixed point o , $G_o = G$. In the general case, it is easy to prove that $G_{g \cdot m} = gG_m g^{-1}$; so *the set of stabilizers of the elements of an orbit is a conjugacy class $[H]_G$ of subgroups of G (H is one of the stabilizers).*

A very simple, but important remark, is that the action $G \xrightarrow{\rho} M$ defines implicitly an action of any strict subgroup $^1 H < G$, by restricting ρ to H (the restric-

¹The traditional notation for subset is $X \subseteq M$ and, for strict subset, $X \subset M$. For subgroups of groups we find convenient to use the less traditional notation $H \leq G$ (or for strict subgroups: $H < G$). This notation recalls also the fact that to be subgroup of a group is a partial order relation (by inclusion) among the subgroups of G .

tion is denoted by $\rho|_H$). When the action $G \xrightarrow{\rho} M$ is restricted to that of a subgroup H :

$$H < G \xrightarrow{\rho} \text{Aut } M : H_m = H \cap G_m. \quad (10)$$

In general the G -orbits split into a disjoint union of H -orbits.

Definition: *orbit type*. Orbits with the same conjugacy class of stabilizers are of the same type.

One such type with G as stabilizer is the set of fixed points. Similarly the orbits with a trivial stabilizer 1 (then all stabilizers of the orbit are 1), are called *principal orbits*.

We shall often use the notation $G : H$ for the type of a G -orbit whose stabilizers are the G -subgroups conjugate to H . For instance a principal orbit can be noted $G : 1$. For a finite set F we denote by $|F|$ its number of elements. When G is finite, the number of elements of an orbit of type $G : H$ is:

$$|G : H| = |G|/|H| \quad (11)$$

For Lie groups, the orbit $G : H$ is a manifold of dimension:

$$\dim(G : H) = \dim(G) - \dim(H). \quad (12)$$

If $\dim(G : H) = 0$, i.e. the orbit has a finite number of points, this number is the quotient of the number of connected components of G and H .

Definition: *stratum*. In a group action, a stratum is the union of orbits of the same type. Equivalently, two points belong to the same stratum iff their stabilizers are conjugate.

When they exist, the fixed points form one stratum and the principal orbits form another one.

The set of strata is called the *stratum space* and is denoted by $M||G$. To belong to the same stratum is an equivalence relation for the elements of M or for those of $M|G$. The set of strata $M||G$ is a (rather small in our applications) subset of the set of conjugacy classes of subgroups of G . Notice that there exists a natural partial order between these conjugacy classes: one is smaller than the other if it contains a group which is a strict subgroup of a group of the other. That gives to $M||G$ a structure of partially ordered set.

As we saw in (10) given an action of G on M , by restriction one has immediately the action on M of any subgroup $H \subset G$. There is a natural (surjective) map

$$(M|H) \longrightarrow M|G. \quad (13)$$

That corresponds to the fact that the orbits of G may split (and generally do) into orbits of H . Beware that there is no natural map between the stratum spaces; indeed the number of conjugacy class of stabilisers is often larger for the larger group. Another interesting case occurs when H is invariant subgroup of G (we write here $H \triangleleft G$, as usual in the mathematical literature on groups).

Indeed there is a natural action of the quotient group G/H on the orbit space $M|H$. This general theorem is very intuitive when H is a G -subgroup of index 2, i.e. $G/H \sim Z_2$: then there are two types of Z_2 orbits on $M|H$, those of one point and those of two points. We shall use several times this theorem, most often in the simplest case.

All the groups we use in this paper are compact Lie groups or finite groups; the latter are a particular case of compact groups: those of dimension zero. There are remarkable theorems on the compact group actions on compact manifolds; Palais (1970) proved that such a differentiable (in short C^1) action is equivalent to an infinitely differentiable (in short C^∞ or "smooth") action. In that case Mostow (1957a, 1957b) proved that the number of strata ($=|M||G|$) is finite and that there exists an orthogonal representation of G on a finite dimensional orthogonal space $^2 V$ containing M in such a way that the action of G on M can be obtained as a restriction of the orthogonal representation of G on V . The maximal strata (i.e. those with maximal symmetries) are closed ³ and (Montgomery, 1957) there exists a unique minimal stratum: it is open dense; we usually call it the *generic stratum*.

In this paper the group actions will be linear representations on a real (orthogonal) vector space V or their restriction to an invariant manifold contained in V . In the next section we will study the invariant polynomials on V . The orbit space $M|G$ can be obtained by equations or inequalities to be satisfied by invariant polynomials, i.e. it is a connected semialgebraic set. In $V|G$, the generic strate is represented by an open dense set whose boundary is the union of algebraic manifolds representing the other strata (of generally different dimensions). So $V|G$ is a connected orbifold. The study of the restriction of the action to an invariant manifold $\Sigma \subset V$ is easy. A good reading on the subject is the memoir (Palais, 1960).

1. Examples.

1. The natural (also called *vector*) representation of $O(n)$ on the orthogonal space V_n has two strata: the origin, a fixed point and a one parameter family of $n-1$ -dimensional spheres S_{n-1} with stabilizers $[O(n-1)]_{O(n)}$. Examples of orbits are shown in Figs. 1,2 for $n = 1, 2$, and 3. Corresponding spaces of orbits are given in Fig. 3.

2. The vector representation of $O(3)$ defines an action of its one dimensional subgroups on S_2 . For C_∞ and $C_{\infty v}$

²Unhappily the proof does not give an upper bound on $\dim(V)$.

³More generally, the union of all strata $\geq$ a given stratum is closed.

FIG. 1. Action of the $O(n)$ group on n -dimensional space defined by its natural (vector) representation. $n = 1, 2$ are shown. For each n there are two types of orbits: one point orbit with the $O(n)$ stabilizer (the origin) and a continuous family of orbits with the $O(n-1)$ stabilizer.

FIG. 2. Action of the $O(3)$ group on 3-dimensional space defined by its natural (vector) representation. Two orbits with the $O(2)$ stabilizer are shown.

FIG. 3. Orbifold for the natural action of the $O(n)$ group on n -dimensional space. Two different strata are indicated by their stabilizers $O(n)$ and $[O(n-1)]_{O(n)}$.

FIG. 4. Action of C_∞ and $C_{\infty v}$ on S_2 induced by natural action of $O(3)$. There are two one point orbits (north and south poles of the sphere) and a one parameter family of circle orbits (each one being a parallel).

FIG. 5. Orbifold for C_∞ and $C_{\infty v}$ group action on S_2 induced by natural action of $O(3)$. The stabilizer for one-point orbits is C_∞ ($C_{\infty v}$) and for generic S_1 orbits is C_1 (C_s) for the symmetry groups C_∞ ($C_{\infty v}$) respectively.

FIG. 6. Action of $C_{\infty h}$, $(D_\infty, \text{ and } D_{\infty h})$ on S_2 induced by natural action of $O(3)$. There are one two-point-orbit (north and south poles of the sphere) with the stabilizer C_∞ , $(C_\infty, C_{\infty v})$, one S_1 circle orbit with the stabilizer C_s , (C_2, C_{2v}) , and a one parameter family of orbits (each one being a pair of circles) with the stabilizer C_1 , (C_1, C_s) .

there are two strata: one of two fixed points (= the two poles), the other containing a one parameter family of circles (the "parallels") with stabilizers 1 and C_s respectively. A coordinate of the one-dimensional orbit space is called the latitude λ with $-90^\circ \leq \lambda \leq 90^\circ$. See Fig 4 for the representation of orbits and Fig 5 for the space of orbits (orbifold).

For $C_{\infty h}$, D_∞ , $D_{\infty h}$, there are three strata: two of one orbit: one contains the two poles (stabilizers C_∞ , C_∞ , $C_{\infty v}$ respectively), the other the equator (stabilizers C_s , C_2 , C_{2v}); the third stratum is the generic one, containing a one parameter family of pairs of parallels with the same absolute value λ of latitude, i.e. $0 < \lambda < 90^\circ$. Fig. 6 gives orbits for these groups.

Notice that for these five groups, the orbit space is a closed line segment. (See Figs. 5, 7.)

3a. Vector representation of O_h , the symmetry group of the cube; see e.g. (Jaric, 1984; Michel and Mozrzymas, 1978). This group contains the reflections through 9 symmetry planes intersecting at the cube symmetry center. These planes fall into two O_h -orbits (for the O_h induced action on the set of 2-dimensional subspaces=planes of the representation space V_3): one orbit contains the three planes P_i , parallel to the faces, the other orbit contains the six planes P'_j , each one containing two opposite edges. Each reflection generates a two element group conjugate

FIG. 7. Orbifold for $C_{\infty h}$, D_{∞} , and $D_{\infty h}$ group action on S_2 induced by natural action of $O(3)$. The stabilizer for two-point-orbit is respectively C_{∞} , C_{∞} , and $C_{\infty v}$. The stabilizer for one circle orbit is C_s , C_2 , and C_{2v} . The stabilizer for two-circle-orbit is C_1 , C_1 , and C_s .

in $O(3)$ to C_s . We denote respectively by $[C_s]_{O_h}$ and $[C'_s]_{O_h}$ the two corresponding conjugacy classes of respectively 3,6 two element subgroups. The group O_h contains three families of rotation axes which are respectively made of 3 axes of rotations by $\pi/2$ (they contain the center of opposite faces), 4 axes of rotations by $2\pi/3$ (they contain opposite vertices), 6 axes of rotations by π (they contain the middle of opposite edges). Hence the existence of seven strata:

- the generic stratum contains all points which do not belong to a symmetry plane: stabilizer 1;
- the two strata whose stabilizers form $[C_s]_{O_h}$ and $[C'_s]_{O_h}$ respectively: they contain all points belonging to a unique symmetry plane: P_i and P'_j respectively;
- the stratum of stabilizers $[C_{3v}]_{O_h}$, it contains all points which are at the intersection of only two symmetry planes both of type P'_j and it is the union of 4 rotation axes minus the origin;
- the stratum of stabilizers $[C_{2v}]_{O_h}$, it contains all points which are at the intersection of only two symmetry planes, one of type P_i the other of type P'_j and it is the union of 6 rotation axes minus the origin;
- the stratum of stabilizers $[C_{4v}]_{O_h}$, it contains all points which are at the intersection of only four symmetry planes, two of type P_i and the other two of type P'_j , that stratum Q is the union of 3 rotation axes minus the origin;
- the maximal stratum contains only one point, fixed by O_h : the origin.

The nine symmetry planes partition the space V_3 into 48 convex cones; any one closed cone can be identified with an orbit space. The corresponding space of orbits is given in Fig. 8.

3b. The action of O_h on S_2 is deduced from the previous action. There are no fixed point. The three maximal strata have for stabilizers: $[C_{4v}]_{O_h}$, $[C_{3v}]_{O_h}$, $[C_{2v}]_{O_h}$ and each contains a unique orbit of 6,8,12 points respectively. The orbit space is a two dimensional orbifold: the surface of a triangle. Each of its three vertices represents the

FIG. 8. Orbifold for O_h group action on 3D-space induced by natural action of $O(3)$. Seven different strata are given by their stabilizers.

FIG. 9. Orbifold for O_h group action on S_2 deduced from its action on 3D-space. Six different strata are given by their stabilizers.

orbit of a maximal stratum; the open edge between the vertices $[C_{4v}]_{O_h}$ and $[C_{2v}]_{O_h}$ represents the one family of 24 point orbits with stabilizers forming $[C_s]_{O_h}$, the other two open edges representing the stratum whose 24 point orbits have $[C'_s]_{O_h}$ as stabilizers; the inside of the triangle represents the $|O_h| = 48$ point orbits of the generic stratum. The corresponding space of orbits is given in Fig. 9.

B. G-invariant functions. Their extrema

As suggested from its title, this subsection contains two parts.

1. Rings of G -invariant functions

Given a n -dimensional linear orthogonal representation on V_n of a compact (or finite) group G , all C^∞ (i.e. indefinitely differentiable) G -invariant functions are C^∞ functions of invariant polynomials (Schwarz, 1965). So we can restrict our study to the ring $\mathcal{P}_n^G$ of invariant polynomials on V_n ($\mathcal{P}_n^G$ is a ring since the sum and the product of invariant polynomials are invariant polynomials). For more details on the structure of $\mathcal{P}_n^G$ see the reviews by Stanley (1979) and Jaric (1984).

We must first recall some results on the action of G on $\mathcal{P}_n$, the ring of polynomials on V_n (they depend on n variables). $\mathcal{P}_n$ is also an infinite dimensional vector space of functions. We denote par $\mathcal{P}_n^{(m)}$ the subspace of homogeneous polynomials of degree m . That is a finite dimensional subspace of $\mathcal{P}_n$:

$$\mathcal{P}_n = \bigoplus_{m=0}^{\infty} \mathcal{P}_n^{(m)}, \quad \dim(\mathcal{P}_n^{(m)}) = \binom{m+n-1}{m}. \quad (14)$$

Let $\vec{v} \in V_n$ and $p \in \mathcal{P}_n$. The action of G on $\mathcal{P}_n$ is defined by:

$$g.p(\vec{v}) = p(g^{-1}.\vec{v}) \quad (15)$$

This equation shows that if the representation of G on V_n contains the matrix $-I_n$, every invariant polynomial must contain only monomials of even degree. It is easy to obtain an invariant polynomial; one simply sums all polynomials of a G -orbit: $q = \sum_{g \in G} g.p(\vec{v})$. But we want a systematic knowledge of $\mathcal{P}^G$. The action defined in (15) transforms the $\mathcal{P}_n^{(m)}$ into themselves; the character $\chi^{(m)}(g)$ of the linear representation of G on $\mathcal{P}_n^{(m)}$ was first given by Molien (1897) one hundred years ago through the generating function:

$$\sum_{m=0}^{\infty} \chi^{(m)}(g) \lambda^m = \det(I_n - \lambda g)^{-1}, \quad (16)$$

where λ is a dummy variable. We label by an index α the different equivalent classes of irreducible representations of the compact or finite group G (with $\alpha = 0$ for the trivial representation) and we denote by $\chi_\alpha(g)$ the corresponding character. Let $c_\alpha^{(m)}$ the multiplicity of the irreducible representation α which appears in the G representation on $\mathcal{P}_n^{(m)}$; when G is finite, its value can be computed from the Molien generating functions (Burnside, 1911; Weyl, 1939):

$$M_\alpha(\lambda) \equiv \sum_{m=0}^{\infty} c_\alpha^{(m)} \lambda^m = |G|^{-1} \sum_{g \in G} \bar{\chi}_\alpha(g) \det(I_n - \lambda g)^{-1}. \quad (17)$$

To extend this formula to Lie groups, one must replace the group average $|G|^{-1} \sum_{g \in G}$ by the integral on the

group $\int_G d\mu(g)$ where $\mu(g)$ is an invariant measure on G whose integral is normalized to 1. The Molien functions are rational fractions (i.e. ratios of polynomials) in λ .

Chevalley (1955) proved for the finite groups generated by reflections the

Theorem Chevalley 1. *The ring $\mathcal{P}^G$ of invariant polynomials of a finite reflection group G acting on the orthogonal space V_n , is a n -variable polynomial ring.*

More explicitly, $\mathcal{P}^G$ is the ring of all n variable polynomials whose variables are n algebraically independent polynomials θ_k , $1 \leq k \leq n$. The degrees d_k of the θ_k are obtained from the Molien function which has the form:

$$M(\lambda) = \frac{N(\lambda)}{D(\lambda)} \text{ with } N = 1, \quad D = \prod_{i=1}^n (1 - \lambda)^{d_i}. \quad (18)$$

Example of O_h natural action on 3D-space. We consider its action defined by its three dimensional vector representation. It is well known (e.g. Michel, 1977) that the values of the three d_k are 2, 4, 6. As noted before these values had to be even since $-I_3$, the symmetry through the origin, belongs to the group. The explicit form of the invariants depends on the choice of basis in V_n .

We choose an orthonormal basis whose coordinates axes are identical to the fourfold rotation axes (orthogonal to the cube faces). Then we can choose:

$$k = 1, 2, 3, \quad \theta_k = \sum_{i=1}^3 x_i^{2k}. \quad (19)$$

The polynomial θ_1 is invariant for every orthogonal group representation. The choice of the other θ 's is not unique. For instance we could choose instead of θ_2 any linear combination $\theta'_2 = \theta_2 + \alpha \theta_1^2$, α real; e.g. for $\alpha = -1$, $\theta'_2 = \sum_{i \neq j} x_i^2 x_j^2$.

Notice that the Laplacien (which appears in the Schrödinger equation) commute with all matrices of the orthogonal representation of a group G . So

$$\Delta \mathcal{P}^{(m)G} \subset \mathcal{P}^{(m-2)G}; \quad (20)$$

remember that $\mathcal{P}^{(0)}$ is the one dimensional space of constants; it carries the trivial representation of G . In the same paper Chevalley (1955) proved the second theorem:

Theorem Chevalley 2. *For a finite reflection group G , the ring $\mathcal{P}$ of the polynomials on V_n is a free module ⁴*

⁴ A module is similar to a vector space except that its scalars do not form a field, but only a ring (not every scalar is divisible by another one $\neq 0$). The property that every vector space has bases extends only to free modules. For a very simple counterexample see equ. (27) in Jaric (1984).

on the ring $\mathcal{P}^G$ of invariant polynomials; its dimension is $|G|$ and it carries the regular representation of G .

For finite groups which are not generated by reflections, the Molien function M has still a denominator of the form (18). The numerator $N(\lambda)$ is a polynomial with positive coefficients:

$$N(\lambda) = \sum_{\delta} \nu_{\delta} \lambda^{\delta}; \quad \nu_{\delta} > 0, \quad N(0) = \nu_0 = 1. \quad (21)$$

For each power δ which appears in this polynomial, there exist ν_{δ} G -invariant linearly independent homogeneous polynomials φ_{α} of degree δ ; of course these polynomials have to be algebraic functions of the n “denominator invariants” θ_k (see below). The ring $\mathcal{P}^G$ is a free module and the $N_0(1)$ polynomials φ_{α} ’s form a basis of it. That is there is a unique way to write any G -invariant polynomial as a linear combination of the φ_{α} ’s:

$$p = \sum_{\alpha=0}^{|N(1)|-1} p_{\alpha}(\theta_k(x_j)) \varphi_{\alpha}(x_j) \quad \text{with } \varphi_0 = 1, \quad (22)$$

where the coefficients p_{α} ’s are n variable polynomials. From now on we shall write this structure of module as:

$$\mathcal{P}^G = P[\theta_1, \theta_2, \dots, \theta_n] \bullet (1, \varphi_1, \dots, \varphi_k). \quad (23)$$

We have to emphasize that this notation represents a stronger structure than that of module. Indeed any polynomial in the φ_{α} ’s is an invariant polynomial and should be written in a unique way as a linear combination of the φ ’s with coefficients in $P[\theta_1, \theta_2, \dots, \theta_n]$. So (23) describes a structure of module algebra, i.e. an algebra whose vector space formed by its elements is replaced by a module of ring of scalars $P[\theta_1, \theta_2, \dots, \theta_n]$ and of basis $\{\varphi_{\alpha}\}$. In the computation of the algebra module it might be useful to check its structure by computing its structure “constants”; they are polynomials in the θ_i ’s:

$$\varphi_{\alpha} \varphi_{\beta} = \sum_{\gamma} p_{\alpha\beta}^{\gamma} \varphi_{\gamma}, \quad p_{\alpha\beta}^{\gamma} = p_{\beta\alpha}^{\gamma}, \quad \text{with } \varphi_0 = 1. \quad (24)$$

Throughout the paper we shall use the notation of (23); the θ_i , ($i = 1, \dots, n$) within the braces are n algebraically independent (“denominator”) invariants and φ_{α} , ($\alpha = 0, \dots, k$) with $\varphi_0 = 1$ are algebraically dependent (“numerator” or auxiliary) invariants which form the basis of the module of invariant polynomials. Given a ring $\mathcal{P}^G$, it can be represented by different modules. For example the obvious equivalence

$$\begin{aligned} \mathcal{P}^G &= P[\theta_1, \theta_2, \dots, \theta_n] \bullet (1, \varphi_1, \dots, \varphi_k) = \\ &P[\theta_1, \theta_2, \dots, \theta_n^2] \bullet (1, \varphi_1, \dots, \varphi_k)(1, \theta_n). \end{aligned} \quad (25)$$

The Molien functions are the same, but to pass from the first form to the second form, the numerator and denominator of the first one are both multiplied by $(1 + \lambda^d)$, where d is the degree of θ_n . That possibility is used in

Appendix B. A similar, but more sophisticated equivalence appears in (90). There is a difficulty: it may happen that M_0 (18) could not be used under its most reduced form with positive coefficients in the numerator. Such a possibility is given by Sloane (1977), (see Eq. (47)), the reduced form cannot represent a module.

By definition an invariant polynomial is constant along an orbit. Given two orbits, there is at least one polynomial of $\mathcal{P}^G$ (the ring of G -invariant polynomials whose variables are the coordinates of the vector space of the linear representation of G) which takes different values on them (see e.g. Michel, 1979). Then that has also to be true for the finite set of generating polynomials $\{\theta_i, \varphi_{\alpha}\}$ which is often called an integrity basis. So one can label the points of the orbit space $V|G$ by the set of values of these polynomials. The number n of different θ_i is equal to the dimension of the orbit space and these n θ ’s form a global system of coordinates of $V|G$ when there are no numerator invariants. The latter, when they exist, resolve the ambiguities left by the value of the θ ’s. As values of $n + k$ real polynomials of n real variables, the coordinates of the orbit space must satisfy polynomial equalities and inequalities; this is summarized by “the orbit space $V|G$ is semialgebraic”. Moreover as image of polynomials on the (connected) orthogonal vector space V , the orbit space $V|G$ is connected.

In the case that G is invariant subgroup of a reflection group G_r and G_r/G is Abelian⁵, Stanley (1977) has given a methodic way⁶ for building the module of invariant polynomials for such subgroup of reflection unitary groups. In the case of orthogonal groups which interest us here, the method is obvious. By the second theorem of Chevalley each nontrivial one dimensional representation of G_r appears once in $\mathcal{P}$. We call them the pseudo-invariants of G_r . We keep among them only those which are invariant for G . They are products of the linear forms whose zeros define the symmetry planes of G_r . For instance for the unimodular subgroup of G_r (i.e. the subgroup of elements of determinant 1), there is only one non trivial numerator invariant: the product of the equations of all symmetry planes; it was known that it is, up to a factor, the Jacobian of the G_r invariants.

Example of C_i natural action on 3D-space. That is the 2 element group generated by $-I_3$, the symmetry through the origin. The smallest reflection group which contains it is the 8 element group D_{2h} whose three symmetry planes are the planes of coordinates. The group D_{2h} has 8 one dimensional inequivalent representations.

⁵That is equivalent to $G'_r \leq G < G_r$ where the “derived group” group G'_r is the group generated by the commutators of G_r .

⁶Very natural to physicist, that method was immediately applied to all finite subgroups of $O(3)$ by Michel (1977). Unhappily the last table of this paper is marred by many misprints; they are corrected by Jaric *et al.* (1984).

Only four of them have character 1 for $-I_3$. They yield the four numerator invariant of C_i . With the convention that the indices i, j, k form a permutation of 1, 2, 3, the Molien function, the denominator and numerator invariant polynomials of C_i are:

$$M_0 = \frac{1 + 3\lambda^2}{(1 - \lambda^2)^3}, \quad \theta_k = x_k^2, \quad \varphi_0 = 1, \quad \varphi_i = x_j x_k. \quad (26)$$

The structure of the module of the C_i invariant functions on the 3D-space corresponding to the Molien function (26) may be written as

$$\mathcal{P}^{C_i} = P[x_1^2, x_2^2, x_3^2] \bullet (1, x_1 x_2, x_1 x_3, x_2 x_3). \quad (27)$$

Example of O natural action on 3D-space. The group O is the rotational (unimodular) subgroup of the group O_h which is the group generated by reflections. The same procedure as for the C_i group enables us to construct the only polynomial φ

$$\frac{D(\theta_1, \theta_2, \theta_3)}{D(x_1, x_2, x_3)} = \varphi \quad (28a)$$

$$\varphi = 24x_1 x_2 x_3 (x_1^2 - x_2^2)(x_2^2 - x_3^2)(x_3^2 - x_1^2). \quad (28b)$$

The polynomial φ is a *pseudo-invariant*⁷ of O_h ; it is the (non-trivial) numerator invariant of O , the unimodular group of O_h .

Instead of smooth invariant functions it might also be useful to consider the field $\mathcal{F}^G$ of invariant rational fractions over V_n . In the chapter XVII of his famous book Burnside (1911) proved that the number of generators of $\mathcal{F}^G$ is either n or $n + 1$. Notice that the numerator and the denominator of an invariant rational function are not necessarily invariant. However we should also point out, as a general theorem, that an invariant rational fraction can always been written as a quotient of invariant polynomials.

For reflection groups this number is n since $\mathcal{F}^G = F[\theta_1, \dots, \theta_n]$. For some groups which are not generated by reflections (for example the group O) we can prove that it is 4. At the same time even for some groups which are not generated by reflections the number of generators is only 3. The group C_i gives such an example:

$$\mathcal{F}_3^{C_i} = F[x_1^2, \frac{x_2}{x_1}, \frac{x_3}{x_1}]. \quad (29)$$

It can be easily verified that all generators for $\mathcal{F}_3^{C_i}$ may always be rewritten as a quotient of invariant polynomials: $x_2/x_1 = x_1 x_2 / x_1^2$ and $x_3/x_1 = x_1 x_3 / x_1^2$.

The group of linear transformations of coordinates of a space V_n , i.e. $GL(n, R)$, transforms polynomials into polynomials. That is not the case of general coordinates

transformations of a smooth manifold M ; they preserve only the properties of smooth functions. But the Schwarz theorem (Schwarz, 1965) shows the interest to consider G -invariant polynomials of the coordinates on M . When the action of G on M has been embedded in an orthogonal representation of G on V_n , it is not difficult to compute, from the module $\mathcal{P}_n^G$ of invariant polynomials on V_n , the module of their restriction on M . Let M , of dimension $n - d$, be defined by d algebraic equations⁸ $q_\rho = 0$. Since M is transformed into itself by G , the q_ρ must be (pseudo-)invariant polynomials. Note that the equation can be replaced by $q_\rho^m = 0$ where m is the smallest integer ≥ 2 such that q_ρ^m is invariant. The simplest situation corresponds to the case when these polynomials q_ρ belong to the ring of scalars of the module, they define an ideal of it; let $\mathcal{Q}$ the corresponding quotient. Then $\mathcal{P}_M^G$ is a module on $\mathcal{Q}$, either with same basis as the module $\mathcal{P}^G$ or smaller if some φ become proportional. The denominator of M_0 of $\mathcal{P}_M^G$ has only $n - d$ factor which is the maximal number of polynomials on V_n algebraically independent on M . That result is easy to verify for the action of O_h and C_i on the sphere S_2 of equation $\theta_1 \equiv x_1^2 + x_2^2 + x_3^2 = r^2$. Let us denote by θ'_2, θ'_3 the polynomials in x_1, x_2 obtained from θ_k , $k = 2, 3$, defined in (19), by replacing their monomial x_3^{2k} by $(r^2 - x_1^2 - x_2^2)^k$. Then $\mathcal{P}_3^{O_h}|_{S_2} = P[\theta'_2, \theta'_3]$, the polynomial ring of all the polynomials in these two variables.

From equation (27) we deduce

$$\mathcal{P}_3^{C_i}|_{S_2} = P[x_1^2, x_2^2] \bullet (1, x_1 x_2, x_1 x_3, x_2 x_3). \quad (30)$$

The corresponding Molien function is $(1 + 3\lambda^2)(1 - \lambda^2)^{-2}$.

The description of the ring of invariant polynomials in terms of basic (numerator) and auxiliary (denominator) polynomials forming the integrity basis is very useful as well from the point of view of the geometrical representation of the space of orbits. The important point is that orbits can be unambiguously labeled by the values of invariant polynomials. In other words, invariant polynomials are coordinates in the space of orbits. The role of basic and auxiliary polynomials is different. We illustrate the geometrical construction on several simple examples.

Let us consider the space of orbits for the O_h group action on S_2 deduced from its natural action on 3D-space. Schematic representation of this orbifold was given in previous subsection (see Fig. 9). The polynomial ring of O_h invariants is generated by two basic polynomials (one of fourth and another of sixth degree) which can be chosen as $\theta_1 = x^4 + y^4 + z^4$ and $\theta_2 = x^2 y^2 z^2$. These two invariant polynomials can be used to label orbits. Figure 10 shows the geometrical form of the orbifold in the space

⁷We call pseudo-invariant of a group G , every quantity transforming as a nontrivial one dimensional representation of G .

⁸In the general case some inequalities might also be necessary, but that will not be needed in this paper.

TABLE II. Strata equations for the O_h group action on S_2 . Basic invariant polynomials $\theta_1 = x^4 + y^4 + z^4$ and $\theta_2 = x^2 y^2 z^2$ are used as coordinates for the orbifold representation.

Stabilizer	Equations and/or inequalities
C_{4v}	$\theta_1 = 1, \theta_2 = 0$
C_{3v}	$\theta_1 = 1/3, \theta_2 = 1/27$
C_{2v}	$\theta_1 = 1/2, \theta_2 = 0$
C_s	$1/2 < \theta_1 < 1, \theta_2 = 0$
C'_s	$\theta_1 = 1 - 2s + 3s^2/2,$ $\theta_2 = s^2(1 - s)/4,$ $0 < s < 1, s \neq 2/3$
1	internal points

FIG. 10. Orbifold for the natural action of the O_h group on S_2 .

of invariant polynomials. Different strata are defined by equalities and inequalities summarized in Table II.

Let consider now another example of C_i natural action on 3D-space. Integrity basis includes in this case three basic polynomial invariants and three auxiliary invariants (see (26)). Basic polynomial invariants can be used to label unambiguously the orbits within any region where all auxiliary polynomials keep their sign. The border of those regions is defined as a set of points where at least one of auxiliary polynomials equals zero. Consequently, the space of orbits can be represented by a set of objects (complex). Each object corresponds to one region with nonzero values of auxiliary polynomials. The border of the region corresponds to zero value of some of auxiliary polynomials. Points of border of different objects should be identified to represent properly the topology of the whole space of orbits. Figure 11 shows the representation of the orbifold as a four body decomposition with identification of side-planes labeled by identical letters. It is a connected orbifold.

FIG. 11. Orbifold for the natural action of the C_i group on three dimensional Euclidean space.

2. Extrema of G invariant functions

Given an action of the compact group G on the manifold M and its extension to the orthogonal representation of G on V_n (Mostow, 1957a, 1957b) and a G -covariant vector field $g.\vec{v}(m) = \vec{v}(g^{-1}m)$, one proves (e.g. Michel, 1971, 1980) that any such vector field $\vec{v}(m)$ is tangent at m to the stratum $S(m)$ of m :

$$\forall g \in G, g.\vec{v}(m) = \vec{v}(g^{-1}m) \Rightarrow \vec{v}(m) \in T_m(S(m)). \quad (31)$$

This condition is empty for the generic stratum. Since any G -invariant function f is constant on orbits, its gradient $\vec{\nabla}f$ is orthogonal to the orbit, so it is in the normal vector subspace orthogonal to the orbit:

$$\forall g \in G, g.f(m) = f(g^{-1}m) \Rightarrow \vec{\nabla}f(m) \in N_m(G.m). \quad (32)$$

This condition is empty for finite G . Since the gradient of a G -invariant function is a G -covariant vector field, we have the

Theorem IIB2a. *The gradients of all G -invariant functions vanish on the orbits which satisfy: $F(m) \equiv T_m(S(G.m)) \cap N_m(G.m) = 0$.*

That occurs when $T_m(S(G.m)) = 0$, i.e. for isolated fixed points and, more generally when the tangent to the stratum is identical to the tangent to the orbit i.e.

Corollary IIB2a. *The gradients of all G -invariant functions vanish on the orbits which are isolated in their strata. These orbits are called critical.*

That is the case when a stratum contains a finite number of orbits then it is closed, since the orbits are closed (as continuous map of the compact group G). The converse of that theorem was also proven by Michel (1971) as well as the next theorem. It was also shown that the action of the stabilizer G_m on a neighborhood of the point

m is equivalent to a linear orthogonal representation of G_m and in the reduction of this representation, the subspace containing the trivial representation corresponds to the manifold $F(m)$ defined in theorem IIB2a.

As we saw, it is equivalent for a stratum to be of maximum symmetry or to be closed; if it contains an infinity of orbits, we have the weaker

Theorem IIB2b. *When a stratum is closed and contains an infinity of orbits, the gradient of each G -invariant function vanishes at least on two orbits of the stratum.*

These orbits might be different for different functions. The proof (first given by Michel (1970), theorem 2 p.133) can be sketched as follows: a closed stratum is compact; every continuous function on a compact has at least one maximum and one minimum; that occurs for the restriction to the stratum of every invariant function on M . Since the gradient of the whole function is tangent to the stratum, on it the zeroes of the gradients of the restriction and of the whole function coincide.

We shall make many applications of these theorems. As we have seen, every G -invariant function is a function of the invariant polynomials. The "numerator polynomials" themselves are algebraic functions of the "denominator polynomial". So the following equation summarizes what we know on the gradient of a G -invariant function:

$$\vec{\nabla} f(m) \equiv \sum_{k=1}^n f_k(m) \vec{\nabla} \theta_k(m) \in F(m), \text{ with } \quad (33a)$$

$$f_k(m) = \frac{\partial f(m)}{\partial \theta_k} + \sum_{\alpha} \frac{\partial f(m)}{\partial \phi_{\alpha}} \frac{\partial \phi_{\alpha}}{\partial \theta_k}. \quad (33b)$$

At m , the gradients $\vec{\nabla} \theta_k(m)$ span F_m ; they all vanish on a critical orbit (since $F(m) = 0$) and no condition is imposed on the f_k 's. What are the general conditions for that gradient to vanish? When $0 < d = \dim F(m) \leq n$, the n f_k 's must satisfy d linear equations; when $d = n$ these equations are $f_k = 0$. Is it possible for f to have no extrema outside the closed strata? Morse theory, or its generalizations, answers this question and yields information on the nature of these extrema.

C. Morse theory.

In this work we also need to apply some results of Morse theory (Bott, 1982; Dubrovin, 1990; Fomenko, 1983; Morse, 1925). Consider a smooth (=infinitely differentiable) real valued function f on a real compact manifold M with a coordinate system ⁹ $\{x_k\}$, $1 \leq i \leq$

$d = \dim M$. If at a point $m \in M$ of coordinates x_k the function satisfies the equations: vanishing gradient, i.e. $\frac{\partial f}{\partial x_i} = 0$, and non vanishing determinant of the Hessian, i.e. $\det \frac{\partial^2 f(x)}{\partial x_i \partial x_j} \neq 0$, we say that it has a non degenerate extremum. Then by a change of coordinates $\{x_i\} \mapsto \{y_i\}$, in a neighborhood of m the function can be transformed into $f = \sum_i \varepsilon_i y_i^2$ with $\varepsilon_i = \pm 1$. The number of signs $-$ is independent from the coordinate transformation and it is called the Morse index μ of this non degenerate extremum: for instance $\mu = 0$ for a minimum, $\mu = d$ for a maximum and the intermediate values correspond to the different types of saddle points. A function on M with all its extrema non degenerate is called a Morse function. Let c_k the number of its extrema of Morse index k ; these numbers are finite¹⁰ and may be used to construct the Morse polynomial $\mathcal{M}_f(t)$ for a Morse function which counts all stationary points of the function f with their indices

$$\mathcal{M}_f(t) = \sum_{k=1}^d c_k t^k; \text{ with } d = \dim(M). \quad (34)$$

More generally the Morse polynomial $\mathcal{M}_f(t)$ for a Morse function on M may be defined as

$$\mathcal{M}_f(t) = \sum_{p \in C(f)} t^{\mu(p)}, \quad \mathcal{M}_f(1) = |C(f)| \quad (35)$$

where the sum is taken over the set $C(f)$ of extrema and $\mu(p)$ is the Morse index of the point p . The polynomial $\mathcal{M}_f(t)$ is the quantitative measure of the critical behavior of f .

The essence of the Morse theory is the relation between the numbers of extrema and the Betti numbers of the manifold M . The Betti number b_k is defined as the rank of the k^{th} homology group of M . Intuitively b_k is the maximal number of k -dimensional submanifolds of M which cannot be transformed one into another or into a submanifold of a smaller dimension; for instance for the sphere S_d of dimension ¹¹ d , $b_0 = b_d = 1$ and all the others b_k vanish.

To formulate Morse inequalities for a given d -dimensional manifold M we introduce the "Poincaré polynomial" $P_M(t)$ whose coefficient of t^k is the Betti number b_k of M :

$$P_M(t) = \sum_{k=0}^d b_k t^k; \text{ with } d = \dim(M). \quad (36)$$

¹⁰If there were an infinite number of extrema on the compact manifold M there would be an accumulation point which would be a degenerate extremum.

¹¹An example of S_d is the boundary of the unit ball in the $d+1$ dimensional Euclidean space.

⁹In general a coordinate system cannot be defined on the whole manifold.

The Euler-Poincaré characteristic χ_M of the manifold M is defined by

$$\chi_M = P_M(t = -1). \quad (37)$$

The Poincaré polynomial of a topological product $M = \times_i M_i$ is the product of the Poincaré polynomials:

$$M = \times_i M_i \Rightarrow P_M(t) = \prod_i P_{M_i}(t). \quad (38a)$$

$$\Rightarrow \chi_M = \prod_i \chi_{M_i}. \quad (38b)$$

For instance the Poincaré polynomial of the manifold $\Sigma = S_2 \times S_2$ has the following explicit form:

$$P_\Sigma(t) = (1 + t^2)^2; \quad (39)$$

$$b_0 = b_4 = 1, \quad b_1 = b_3 = 0, \quad b_2 = 2,$$

$$\chi_\Sigma = 4.$$

Using the Poincaré polynomial of the manifold, $P_M(t)$, and the Morse polynomial $\mathcal{M}_f(t)$ for a Morse function f we can formulate the relations between the Betti numbers and the numbers of stationary points of the function f . The precise statement is as follows.

Morse inequalities. For every Morse function f there exists a polynomial $Q_f(t) = q_0 + q_1 t + \dots$ with *non negative coefficients* such that

$$\mathcal{M}_f(t) - P_M(t) = (1 + t)Q_f(t). \quad (40)$$

This statement may be rewritten in terms of d inequalities

$$0 \leq \ell < d: \quad \sum_{k=0}^{\ell} (-1)^{\ell-k} (c_k - b_k) \geq 0 \quad (41a)$$

$$\Rightarrow c_k \geq b_k. \quad (41b)$$

and one equality

$$\sum_{k=0}^d (-1)^k (c_k - b_k) = 0 \Leftrightarrow \sum_{k=0}^d (-1)^k c_k = \sum_{k=0}^d (-1)^k b_k \stackrel{\text{def}}{=} \chi_M, \quad (42)$$

where χ_M is the Euler Poincaré characteristic of the manifold M . The inequalities (41b) are *not* equivalent to Morse inequalities (41a), but they give lower bounds to the number of extrema of a Morse function.

For the manifold Σ , taking into account (39) Morse theory implies for Morse functions on Σ

$$c_0 \geq 1, \quad (43a)$$

$$c_1 - c_0 \geq -1, \quad (43b)$$

$$c_2 - c_1 + c_0 \geq 3, \quad (43c)$$

$$c_2 - c_3 + c_4 \geq 3, \quad (43d)$$

$$c_3 - c_4 \geq -1, \quad (43e)$$

$$c_4 \geq 1. \quad (43f)$$

In the absence of any symmetry requirements many sufficiently good manifolds allow the existence of a so-called *perfect Morse function* which reduces all Morse inequalities into equalities. In other words for the perfect Morse function $Q_f(t) = 0$, i.e. $\mathcal{M}_f(t) = P_M(t) \sim c_k = b_k$. In particular, the number of stationary points $|C(f)|$ of a perfect Morse function f equals the sum of Betti numbers ($= P_M(1)$). When a finite symmetry group G acts on the manifold M , there are further requirements on the c_k 's of G -invariant Morse function: all points of a G -orbit should be simultaneously either extrema with the same index or not be extrema. Some simple physical applications of the Morse theory under the presence of symmetry which are close in spirit to the present analysis were given by Michel and Mozrzymas (1978) and Zhilinskii (1989a, 1989b).

As we saw in subsection IIB, very often the group action itself insures (Corollary IIB2a) that several orbits (the critical orbits) should be stationary for any G -invariant function f . If apart from that there exist closed strata (those with maximal symmetry) and if the orbits they contain are not all critical, then Theorem IIB2b applies and requires to any function at least two orbits of extrema in these strata. In any case, among all invariant Morse functions there exist some of them with the minimal possible number of extrema. We will call such functions *the simplest Morse type functions*. We can still introduce the natural measure of the complexity of a given Morse type function just by counting the total number of stationary points.

In case of a symmetry realized by the effective action of a continuous compact group, most of the orbits are themselves continuous compact manifolds. The situation becomes more complicated when some of these orbits are orbits of extrema of an invariant function f : indeed these extrema of f are degenerated along the directions tangent to the orbit. So the Morse theory in its original form is not applicable.

There exists an extension of Morse theory for G -invariant function with non zero dimensional orbits of extrema. References (Atiyah, 1982; Bott, 1982; Fomenko, 1983) give the basic mathematical facts with some ideas of physical applications. Analysis of one particular physical problem using this technique is made, for example, by Kirwan (1988).

First of all we extend the concept of non-degeneracy of a function f defined over the manifold M . If N is a connected submanifold of M , it will be called a *nondegenerate stationary manifold* for f if and only if at every point of N , $df = 0$ and the Hessian is nondegenerate on the normal bundle.

It is natural to extend the notion of the Morse index to nondegenerate stationary manifolds by counting the number of negative eigenvalues of the Hessian on the normal bundle. A function f will be called non-degenerate Morse Bott type function if its set $C(f)$ of extrema is a union of non-degenerate stationary manifolds and non degenerate isolated extrema. These isolated extrema will

also be called stationary points of the function, as it is often done in mechanics.

Let now describe shortly what should be done with Morse theory to take into account *a priori* symmetry of a function f under the action of a (continuous) compact Lie group G on a manifold M . If the action is free (i.e. all stabilizers $G_m = 1$ so there is only one stratum, and all its orbits are principal) the solution is very simple. In this case the orbit space M/G is itself a manifold and we can apply the usual Morse theory to the corresponding function f/G defined over M/G . Unfortunately this is not the case for all examples studied in the present paper. The action of the symmetry group on the phase space Σ is not free.

To extend Morse inequalities on the case of functions possessing nondegenerate stationary manifold there are two possibilities. There exist more sophisticated Morse inequalities written in terms of usual homology groups for the whole manifold M and for stationary (non degenerate) submanifolds. We have also to consider Poincaré polynomial $P_{C_\alpha}(t)$ for each connected component C_α of the set of stationary points. These last polynomials are needed to write down the polynomial counting stationary points and stationary manifolds of a Morse-Bott function, $\mathcal{M}_f(t)$

$$\mathcal{M}_f(t) = \sum t^{\mu(C_\alpha)} P_{C_\alpha}(t), \quad (44)$$

Here $\mu(C_\alpha)$ is the Morse index of the nondegenerate stationary submanifold C_α . If C_α is an isolated stationary point the corresponding Poincaré polynomial reduces to 1. If for example, C_α is a one-dimensional sphere S_1 , such a stationary submanifold is counted by a $(1+t)$ polynomial.

The Morse inequalities now reads

$$\sum t^{\mu(C_\alpha)} P_{C_\alpha}(t) - P_M(t) = (1+t)Q_f(t), \quad (45)$$

where all coefficients of the polynomial $Q_f(t)$ are non negative. Another way of extension of Morse theory to G -invariant function is based on the possibility to replace everywhere the usual homology by their equivariant analogs. The following theorem is valid

The equivariant Morse inequalities. For any nondegenerate G invariant f on the compact manifold M , the Morse inequalities hold in the equivariant sense

$$\mathcal{M}_f^G(t) - P_t^G(M) = (1+t)Q_f^G(t), \quad (46)$$

where all coefficients of the polynomial $Q_f^G(t)$ are non negative. In spite of the fact that this extension seems to be rather simple, the non-triviality lies in the fact that equivariant homology should be calculated. We will not go here into equivariant theory (see appendix D for further examples) but just note that naturally the definition of the perfect function may be given in the equivariant sense. Namely, the function is perfect in the equivariant sense if $Q_f^G(t)$ is zero. As it was remarked by Bott, the

function may be perfect in the equivariant sense but not in the normal sense. That is why we prefer to use the notion of the simplest Morse-Bott function in the case of continuous symmetry as well and to use the complexity measure by counting the number of connected components of the set of stationary points of the function.

It should be noted that even under the presence of continuous symmetry group the symmetry group action may result in a set of critical orbits which are the isolated points and the simplest Morse-Bott function may possess in such a case only isolated stationary points.

Several examples studied in the next section show the presence of critical orbits which are in fact stationary manifolds ($O(3)$, D_∞ , $D_{\infty h}$ actions on Σ). At the same time for such continuous symmetry groups as C_∞ , $C_{\infty h}$, and $C_{\infty v}$ acting on Σ the critical orbits are the isolated points only.

We can define now the simplest Morse (Morse-Bott) type functions as a class of functions possessing the minimal number of nondegenerate stationary points (or manifolds). This minimal number can not be less than the number of critical orbits but it is allowed to be larger. To give the classification of Morse (Morse Bott) type functions due to complexity of the system of stationary points we introduce the measure of complexity to be the number of stationary points and the number of stationary manifolds excluding those associated with critical orbits. If the number of critical orbits is less than the number of stationary points due to the topological structure neglecting the symmetry (we assume that the perfect Morse type function exists on the manifold considered if there are no symmetry restrictions) it is necessary to subtract the sum of Betti numbers from the total number of stationary points to find the complexity index.

Further classification of the Morse type functions within one class of the same complexity (i.e. with the same number of stationary points (manifolds)), takes into account possible different distributions of stationary points (manifolds) over strata or within one stratum.

Now the general aim of the qualitative analysis may be formulated:

- i) To describe qualitatively different generic Hamiltonians invariant under given symmetry group.
- ii) To describe possible qualitative generic changes of Hamiltonians occurring under the variation of a given number of parameters.
- iii) To relate qualitative changes of classical functions with corresponding changes of quantum Hamiltonians.

D. Qualitative analysis for classical limits.

The qualitative description (Gilmore, 1981; Poston, 1978; Smale, 1970; Thom, 1972) is based primarily on concepts of topology and symmetry. The key notion of the qualitative analysis is "structural stability" which means that the qualitative description obtained is stable

with respect to small variations of the model. It assumes that we study some generic situation but this generic behavior may be restricted to some special class (some a priori symmetry requirements may be imposed by physical requirements).

The idea of qualitative (topological) analysis of mechanical systems was initiated by Poincaré (1879) and Lyapounov (1892) in the 19-th century. A program of topological analysis of simple mechanical systems with symmetry was formulated by Smale (1970). Its partial concrete realization for the three body problem culminates the classical book of Abraham and Marsden (1978). During the several last decades the formal abstract theory was enormously developed. In particular many mathematical results concerning influence of topology and symmetry on general dynamical systems and on Hamiltonian systems were formulated. Apart from some purely abstract models the most important applications of these developed mathematical techniques concern field theory, particle physics, nuclear physics and even other branches of science which are apparently rather far from physics (biology, ...). At the same time applications to quantum molecular physics problems are still relatively rare except, perhaps, for quantum chaos. Nevertheless the study of quantum problems very often may be reduced to the analysis of corresponding classical objects especially for highly excited quantum systems. The transformation of quantum problem into its classical limit is physically meaningful for large quantum numbers which play the role of the inverse of the Planck constant $\hbar^{-1}$ under going to the classical limit (Perelomov, 1986; Zhang, 1990). Very often in molecular problems this high quantum number limit is really accessible. We can cite the analysis of rotational spectra up to $J \sim 100$ (Harter, 1978, 1988) and observation of Rydberg states of H_3 molecule with $n \sim 100$ (Bordas and Helm, 1992).

The reason why qualitative study of highly excited molecular systems through an analysis of classical limit is not so popular may probably be explained as follows. Molecular systems are described by a relatively simply formulated Hamiltonians with known potentials and the description of intra-molecular dynamics is considered often as a numerical problem whose solution depends mainly on the development of the computer facilities. From the other side, the experimental study mainly due to the development of high and super-high resolution laser spectroscopy enables one to collect an enormous amount of information about spectral lines in different regions of spectra with the precision of about 10^{-7} - 10^{-15} in relative units. Thus, the spectroscopists are mainly concerned with the use of some quantitative phenomenological models which enable one to interpret and to reproduce observed spectra with high accuracy compatible with the experimental precision. The global qualitative features are considered sometimes as amazing facts which may be related to specific features of a single concrete model and are not recognized as universal.

To support this point of view let us just cite an ex-

ample: the description of the formation of the rotational cluster structure for isolated molecules. The presence of six-fold and eight-fold rotational clusters for spherical top molecules with cubic point group symmetry was discussed in 1977 by Fox *et al.* (1977) [see also Biedenharn and Louck (1981)] on the basis of extensive numerical calculations for one concrete effective rotational operator (which is defined by symmetry arguments nevertheless). In spite of the fact that such clustering was remarked and even explained by simple classical arguments earlier (Dorney, 1972; Kirschner, 1973; Michelot, 1975), it was only after receiving a huge amount of numerical results that the simple classical (or quantum) description of the clustering was fully explored (Harter, 1977, 1978, 1988; Patterson, 1977; Zhilinskii, 1979). The essence of the clustering phenomena is the symmetry breaking effect related to the symmetry group action on the phase space of the problem considered. The type of clustering depends on the topology of the phase space and on the symmetry group action on this space (Michel, 1979; Zhilinskii, 1989b, 1996; Sadovskii, 1993a).

Whereas the importance of the group action analysis for different fields of physics and its relation to different kinds of phase transitions and spontaneous symmetry breaking effects was fully demonstrated in a series of papers by L. Michel (1972, 1979, 1980) the applications to realistic molecular examples was made significantly later.

We will use in this paper the general scheme of the qualitative analysis to study the peculiarities of Rydberg problems. The steps that we will follow can be summarized as follows.

- (A) Construction of a classical limit Hamiltonian system for a given model quantum Hamiltonian. At this stage we construct a classical phase space and a classical analog for the Hamiltonian. Two situations are quite different from the point of view of subsequent analysis: the obtained classical phase space is compact or not. For a compact phase space we can make a global analysis and deduce possible numbers of stationary points of Hamiltonian functions from the topological characteristics of this space. For a non-compact phase space we are restricted to a local analysis around stationary points.
- (B) Analysis of the action of the invariance group of a particular problem on the phase space.
- (C) Qualitative classification of corresponding classical Hamiltonian functions for a particular problem. This step assumes introduction of some qualitative equivalence between dynamical system or their Hamiltonians. Several levels of qualitative, or topological, equivalence were introduced and studied for classical systems (Abraham, 1978). The finest classification is based on the phase portrait equivalence. We use much cruder equivalence relations. First of all, for two classical systems to be qualitatively equivalent their phase spaces should be

at least topologically equivalent. A more detailed classification of phase spaces takes the symmetry of the Hamiltonian into account. This is especially important for molecular systems which have many different invariance groups. Starting from the invariance group of an initial molecular problem we can find the classification of the points on the classical phase space by their symmetry, i.e. define the *group action* on the phase space. At this point we introduce the equivalence relations which preserve the group action on the phase space.

A further step involves the comparison of the Hamiltonian functions defined over the phase space by their systems of stationary points. Taking into account the action of a symmetry group, two Hamiltonian functions are considered to be equivalent if their numbers of stationary points of any index are the same. Moreover, we compare the numbers of stationary points of the same index and of the same local symmetry.

- (D) Analysis of bifurcations, or possible qualitative changes, of stationary points which occur due to the variation of some physical characteristics, such as strict or approximate integrals of motion. The latter are considered as parameters of the model Hamiltonian under study.
- (E) Re-interpretation of the qualitative features of the classical Hamiltonian function for the initial quantum operator.

This scheme was realized on several examples. We give below the summary of results with relevant references to demonstrate how the scheme given above works in some simple concrete situations before going to the main subject of the present paper the qualitative description of Rydberg states.

1. Purely rotational Hamiltonian

The most simple example is the purely rotational problem mentioned above.

- (A) Rotational quantum Hamiltonian is written in terms of angular momentum operators J_α which are the generators of the $so(3)$ algebra. The corresponding classical limit is associated with a classical function defined over the two dimensional phase space and depending on the absolute value of the angular momentum as a parameter. Two dynamic classical variables may be considered as two angles giving the orientation of the angular momentum vector $\mathbf{J}$ with respect to the molecular fixed coordinate system. So the classical phase space for purely rotational problem is a two dimensional sphere S_2 and a Hamiltonian is a function defined over S_2 and depending on J .

- (B) Even if the molecule considered possesses no symmetry the rotational Hamiltonian is still invariant with respect to the inversion of the space because it is constructed from the angular momentum operators which are themselves invariant under inversion. This is a consequence of the time reversal invariance which is a strict invariance for an isolated systems under the absence of weak interactions. So the rotational Hamiltonian is always invariant with respect to the C_i group. The action of the C_i group on the S_2 space gives the only one type of orbits - two point orbits with the trivial C_1 group as a stabilizer. There is only one stratum and the space of orbits is the RP_2 space (two dimensional real projective space) which may be represented as a S_2 sphere with the identification of each pair of diametrically opposed points. If molecule has point group symmetry G the invariance group of the rotational Hamiltonian G_1 is the minimal group which includes both G and C_i groups as subgroups. For tetrahedral molecules with T_d point symmetry group the invariance group of the rotational Hamiltonian is the O_h group. Its action on the S_2 sphere was described earlier (see subsection IIA 1 and Fig.9 in particular).

- (C) For the non-symmetrical molecules the simplest Morse type Hamiltonian function should possess two equivalent minima, two equivalent maxima, and two equivalent saddle points. The position of these stationary points is not fixed because the action of the C_i group gives no critical orbits. For tetrahedral or cubic molecules (with the molecular point symmetry groups T_d , O , O_h) any Morse type function possesses at least 26 stationary points due to the presence of three critical orbits (six-point C_{4v} orbit, eight-point C_{3v} orbit, and 12-point C_{2v} orbit) of the O_h group action on the S_2 sphere. The simplest Morse type function exists with the only 26 stationary points. Moreover it follows immediately that C_{4v} and C_{3v} orbits are minima and maxima whereas C_{2v} orbit corresponds to saddle points.

- (D) Under the variation of the unique integral of motion (the absolute value of the angular momentum J) for non-symmetrical molecule only one type of bifurcations is possible. This is a non-symmetrical nonlocal bifurcation $C_1^\pm$ resulting in the appearance (+) or disappearance (-) of a stable-unstable pair of stationary points with the trivial stabilizer [we follow the notations of Sadovskii and Zhilinskii (1993a)]. For tetrahedral molecules all five different types of symmetrized bifurcations are possible. Rather detailed description of qualitatively different types of Morse functions over S_2 manifold under the presence of the O_h symmetry group was given by Sadovskii and Zhilinskii (1993a) (see the Table V of that reference in particular) and by Zhilinskii, Brodersen, and Madsen (1993) as well.

- (E) As soon as we know the qualitatively different classical Hamiltonians functions we can predict the corresponding qualitatively different patterns of energy levels for quantum analogs. It is sufficient to apply the simplest semi-classical approach to get the energy level patterns near the stable stationary points. For non-symmetrical molecules there are two equivalent minima and two equivalent maxima for the case of the simplest Morse type Hamiltonian. It means that for sufficiently high J value (to ensure the proper classical limit) there is a sequence of quasi degenerate doublets with the corresponding quantum wave functions localized near two equivalent minima and another sequence of quasi degenerate doublets with the corresponding quantum wave functions localized near two equivalent maxima. Close to the energy corresponding to two equivalent saddle points (separatrix in the classical limit) there is some intermediate region with the absence of clusters and with the delocalised along the separatrix wave functions. For tetrahedral molecules the supposition about the simplest form of the Hamiltonian as a Morse type function yields the following qualitative pattern of energy levels: the sequence of six fold clusters with corresponding wave functions localized near the C_{4v} orbit, the sequence of eight fold clusters with corresponding wave functions localized near the C_{3v} orbit.

2. Vibrational polyads

Another well studied example is the description of vibrational polyads formed by several (quasi)degenerate vibrations. Vibrational polyads are groups of degenerate or quasidegenerate vibrational levels which are frequently present in vibrational energy spectra due to resonances between different vibrational frequencies.

- (A) The effective quantum Hamiltonian giving the description of the internal structure of vibrational polyads may be easily written by starting with the N dimensional isotropic harmonic oscillator and imposing the condition of the constant number of the vibrational quanta. This problem was analyzed in details by Child (1984), Jaffé (1980), Kellman (1995), Lawton (1979), Mills (1985). The classical limit in this problem has non trivial topological properties (Zhilinskii, 1989a). For N quasi-degenerate vibrations we have $2N - 2$ -dimensional phase space which is in fact a CP_{N-1} complex projective space. For two quasi-degenerate vibrational modes due to the equivalence $CP_1 \sim S_2$ we have again the two dimensional sphere S_2 as a phase space.
- (B) To find the group action on the phase space it is necessary first to define the group image of the

molecular symmetry group on the representation spanned by the dynamical variables of the problem considered. The symmetry group of the effective Hamiltonian is a subgroup of the molecular symmetry group whose concrete form depends on the symmetry types of the vibrational modes considered.

- (C) Sometimes even for highly symmetrical molecules the invariance group for effective Hamiltonian may be trivial (no symmetry at all). In this case the simplest Morse type function possesses the minimal number of stationary points imposed by the topology of the manifold. For the two quasi-degenerate vibrations with the S_2 manifold as a phase space the simplest Morse type function has one minimum and one maximum whose positions are not fixed. The same minimal number of stationary points (two) is present for two mode polyads under the presence of the C_2 symmetry. This is rather typical case of two quasidegenerate modes (symmetric and antisymmetric stretching) of AB_2 molecules with C_{2v} point symmetry group.
- (D) The analysis of possible bifurcation of the Hamiltonian function predicts qualitative changes in the energy level patterns within the vibrational polyads and the localization of corresponding vibrational functions. In particular, the very much discussed transition between normal and local modes (Lawton, 1979; Child, 1984) may be easily interpreted as a result of a bifurcation from the simplest Morse type Hamiltonian to more complicated one possessing extra stationary points (Sadovskii and Zhilinskii, 1993a). Atomic analogs of local and normal modes were discussed by Milligan and Farrelly (1993).

3. Dynamical symmetry of Rydberg states.

Now we can formulate the classical limit construction for the Rydberg problem studied. General scheme of the classical limit construction is based on the method of generalized coherent states (Perelomov, 1986; Cavalli, 1985; Zhang, 1990). This formal construction starts with introducing a dynamical algebra g whose generators play the role of the dynamic variables of the problem. The Hamiltonian itself in this case is considered as an operator in the enveloping algebra. For the Rydberg problem the dynamic algebra is the $so(4)$ algebra with $\mathbf{J}$ and $\mathbf{K}$ generators (see section I, eqs. (4)). An equivalent way to represent the same algebra is to use two commuting vector operators $\mathbf{J}_1$ and $\mathbf{J}_2$. In any of these representations two important relations (5) restrict the space of the dynamic variables variation to four dimensional space. The geometrical significance of this space is clearly seen in the $\mathbf{J}_1, \mathbf{J}_2$ representation. Different points of the classical limit phase space are in one to one correspondence

with orientations of two vectors $\mathbf{J}_1, \mathbf{J}_2$. This space is the topological product of two two-dimensional spheres $S_2: S_2 \times S_2$. We will note this space as Σ . It plays the essential role in all the subsequent analysis.

Arbitrary effective Hamiltonian which gives the description of the internal structure of Rydberg multiplets may be written in the classical limit as a function defined over Σ (the classical phase space for the Rydberg problem). Following steps of the qualitative analysis of the Rydberg problem may be concretized now as follows.

i) Study of the action of the invariance group on Σ , classification of orbits and strata. Finding the critical orbits. (See Section III.)

ii) Application of Morse theory to the complexity classification of function defined over Σ under the presence of the invariance symmetry group. (See Section IV.)

iii) Construction of an arbitrary effective Hamiltonian in terms of expansion over integrity basis. Representation of classical Hamiltonians near critical manifolds and the qualitative description of the corresponding quantum energy level patterns and wave-functions. (See Sections IV, V.)

III. GROUPS AND THEIR ACTIONS APPROPRIATE FOR THE RYDBERG PROBLEM

The dynamical symmetry group of hydrogen atom Rydberg states is $O(4) \wedge T$, where T is the time reversal.¹² For other physical systems this group can be used as first approximation: only a subgroup of it is the exact symmetry. In the beginning of this section we build the group $O(4) \wedge T$ and the phase space Σ of Rydberg problems. The rest of the section is devoted to the study of the action of the $O(4) \wedge T$ subgroups on Σ .

A. Structure of $O(4)$.

As we have seen in the introduction, the quantum Hamiltonian of the hydrogen atom commutes with the 6-dimensional Lie algebra described in the equations (4) and recognized under the form (7) as the Lie algebra of $SU(2) \times SU(2)$. But many non isomorphic Lie groups have the same Lie algebra, e.g. $SO(3) \times SO(3)$, $O(3) \times O(3)$, $SU(2) \uparrow 2$ (defined in (58)), $SO(4)$ and $O(4)$ as shown in equations (55) and (60). There is some ambiguity for choosing between these different groups; but a non connected one is definitely richer and better

adapted to the physics, so we choose here $O(4)$ as an approximate symmetry of Rydberg states. (Time reversal will be added in subsection III B 1.)

We begin by studying $SO(4)$. The connected orthogonal groups $SO(n)$ for $n > 2$ have a double covering call $Spin(n)$. For $n = 3$, $SO(3)$ is the group of rotations in the 3-dimensional space and its spin group $Spin(3) = SU(2)$, the group of 2×2 unitary matrices with determinant 1. The relation between these two groups is the homomorphism $SU(2) \xrightarrow{\sigma} SO(3)$. The image of this homomorphism is the full $SO(3)$ group and its kernel is the center $\{I_2, -I_2\}$ of $SU(2)$. We denote it by $Z_2(-I_2)$. This whole information can be expressed in one line way¹³:

$$1 \longrightarrow Z_2(-I_2) \longrightarrow SU(2) \xrightarrow{\sigma} SO(3) \longrightarrow 1 \quad (47)$$

This notation is an *exact sequence*. A less explicit notation is $SO(3) = SU(2)/Z_2(-I_2)$.

To understand better the interrelations between different Lie groups having the same $su(2) \times su(2)$ algebra we give below their realization as groups of transformations of the quaternions.

The elements $q \in \mathbb{Q}$, the quaternion field, can be represented by the 2×2 matrices [e.g. Duval (1964)]:

$$q = q_4 I + i q_1 \tau_1 + i q_2 \tau_2 + i q_3 \tau_3, \quad (48)$$

$q_\alpha \in \mathbb{R}$, $\alpha = 1, 2, 3, 4$, where the three Hermitian matrices $\tau_k = \tau_k^*$ are the Pauli matrices:

$$\tau_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \tau_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \tau_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (49)$$

Notice that q is not Hermitian. Indeed $q^* = \tilde{q}$ with

$$\tilde{q}_4 = q_4, \quad \tilde{q}_1 = -q_1, \quad \tilde{q}_2 = -q_2, \quad \tilde{q}_3 = -q_3. \quad (50)$$

We verify:

$$qq^* = q^*q = |q|^2 I, \quad \text{with } |q|^2 = \sum_{\alpha=1}^4 q_\alpha^2 \quad (51)$$

where $|q| = |q^*|$ is called the norm of the quaternion q . Notice that $|q| > 0$ when $q \neq 0$ and $|qq'| = |q||q'|$. That last property can be checked from (51) or from:

$$|q|^2 = \det q. \quad (52)$$

¹²the symbol $\wedge$ is a shorthand for defining the groups generated by the groups or group element written on each side of this symbol.

¹³The exact sequences used here are all of the type $1 \longrightarrow A \longrightarrow B \longrightarrow C \longrightarrow 1$. They mean A is the invariant subgroup of B and $C = B/A$. This notation is now currently used even in undergraduate studies. For more details see e.g. Michel (1980).

Equation (51) shows that the set of quaternions form a dimension 4 orthogonal space with the scalar product:

$$(q, q') = \frac{1}{2} \text{tr } qq'^* = \frac{1}{2} \text{tr } q'q^* = \sum_{\alpha=1}^4 q_{\alpha} q'_{\alpha}. \quad (53)$$

By definition, the group $SU(2)$ is the multiplicative group of 2×2 unitary matrices of determinant 1. That group is realized by the multiplication of the quaternions of norm $|q| = 1$; indeed (52) shows that $\det q = 1$ and, from (51), q is unitary. Moreover the manifold of $SU(2)$ elements, i.e. the quaternions of norm 1, is S_3 , the unit sphere in the dimension 4 orthogonal space of $\mathcal{Q}$.

The group $SU(2) \times SU(2)$ acts linearly on the quaternions by:

$$(u, v) \in SU(2) \times SU(2), (u, v) \cdot q \stackrel{\text{def}}{=} uqv^*. \quad (54)$$

This action preserves the quaternion norm. Moreover it is *transitive* on the set of quaternions of a given norm: indeed the quaternion $|q|I$ is transformed into the arbitrary quaternion q of the same norm by $u = q|q|^{-1}$, $v = I$. This shows the existence of a group homomorphism:

$$SU(2) \times SU(2) \xrightarrow{\theta} O(4); \quad (55a)$$

$$\text{Im } \theta = SO(4), \text{ Ker } \theta = Z_2(-I, -I). \quad (55b)$$

Indeed, θ is continuous so its image is connected; the transitivity property we have just established requires $\text{Im } \theta = SO(4)$. By definition $\text{Ker } \theta$ is the set of group elements acting trivially on $\mathcal{Q}$; they are $u = v = \pm I$.

The stabilizer of the quaternions of the form $q_4 I$ is made of the elements $v = u$; one calls it the diagonal subgroup $SU(2)^d \subset SU(2) \times SU(2)$. Moreover $SU(2)^d$ transforms into itself the 3 dimensional subspace of quaternions orthogonal to I (their trace vanishes); that establishes the well known homomorphism $SU(2)/Z_2 = SO(3)$.

We shall consider the 4×4 orthogonal matrix

$$s = \begin{pmatrix} -I_3 & 0 \\ 0 & 1 \end{pmatrix}, \quad s^2 = I, \quad \det s = -1. \quad (56)$$

It is the inversion through the origin for the subgroup $O(3) \subset O(4)$ which leaves fixed the coordinate q_4 ; as (50) shows, it transforms q into q^* . Every element of $O(4)$ not in $SO(4)$ is of the form $s\theta(u, v)$. Let us study the induced action of these elements on $SU_2 \times SU_2$ from their known action on every quaternion q :

$$s\theta(u, v)s^{-1} \cdot q = s\theta(u, v) \cdot q^* = s \cdot (uq^*v^*) = vqu^*; \quad (57)$$

it is the permutation of the two factors in $SU_2 \times SU_2$. So we are led to consider the wreath product $SU_2 \uparrow 2$ which is defined as the semi-direct product:

$$SU_2 \uparrow 2 \sim (SU_2 \times SU_2) \rtimes Z_2(P), \quad (58)$$

where $Z_2(P)$ denotes the group of permutations of the two factors of $SU_2 \times SU_2$. To summarize, we have established the two exact sequences

$$1 \longrightarrow Z_2^d(-I_2, -I_2) \longrightarrow SU_2 \times SU_2 \xrightarrow{\theta} SO(4) \longrightarrow 1, \quad (59)$$

$$1 \longrightarrow Z_2^d(-I_2, -I_2) \longrightarrow SU_2 \uparrow 2 \xrightarrow{\theta'} O(4) \longrightarrow 1. \quad (60)$$

Notice that $SO(4)$ and $O(4)$ have a two element centre generated by the matrix $-I_4$. Eq. (59) shows that $SU(2) \times SU(2) = Spin(4)$. Its elements can be labelled by a pair of indices $u_1, u_2 \in SU(2)$. Then $\theta(u_1, u_2)$ defines an orthogonal matrix $g \in SO(4)$

$$SO(4) \ni g \sim \theta(u_1, u_2). \quad (61)$$

The elements of $O(4)$ are either of the form g or sg with s defined in (56).

The irreducible representations of a direct product of groups are the tensor product of their irreducible representations. It is customary to label the irreducible representations of $SU(2)$ by j , $0 \leq 2j \in \mathbb{Z}$; so the irreducible representations of $SU(2) \times SU(2)$ are usually labeled by the pair (j_1, j_2) . They have the dimension $(2j_1 + 1)(2j_2 + 1)$. The representations of $SU(2) \uparrow 2$ are labelled by $(j_1, j_2) \oplus (j_2, j_1)$ (of dimension $2(2j_1 + 1)(2j_2 + 1)$) when $j_1 \neq j_2$. When $j_1 = j_2$ this representation becomes reducible into the direct sum of two reducible representations $(j, j)^{\pm}$ which are respectively symmetric and antisymmetric for the permutation of the two $SU(2)$ factors. Among all representations those with $j_1 \pm j_2 \in \mathbb{Z}$ form the set of irreducible representations of $O(4)$. They are faithful when j_1, j_2 are both half integers; when j_1, j_2 are both integers their image is that of the "adjoint" group of $O(4)$, that is the quotient $O(4)/Z_2(-I_4)$ of $O(4)$ by its center. It is easy to see that it is isomorphic to $SO(3) \uparrow 2$. This can be summarized by

$$1 \longrightarrow Z_2(-I_4) \longrightarrow O(4) \xrightarrow{\vartheta} SO(3) \uparrow 2 \longrightarrow 1. \quad (62)$$

The equation (8) shows that the only irreducible representations carried by the n^2 dimensional space of state vectors of a Rydberg multiplet have $j_1 = j_2$. As we shall show they are $(j, j)^{\pm}$ with $n = 2j + 1$. It is why we say that it is $O(4)$ and not $SU(2) \uparrow 2$ which is the symmetry group of the Rydberg problem. Remark that these representations are faithful only when j is half integer. That is the case of $(\frac{1}{2}, \frac{1}{2})^+$, the vector representation (i.e. that of dimension 4) of $O(4)$ that we have studied in this subsection.

B. The adjoint representation of $O(4)$; induced action on $\Sigma = S_2 \times S_2$.

The adjoint representation of $O(4)$ is $(1, 0) \oplus (0, 1)$; indeed, by definition, it is the representation of $O(4)$ on

the 6-dimensional vector space of its Lie algebra. We denote by $V = V_1 \oplus V_2$ this space direct sum of two 3-dimensional vector spaces. The operators $\mathbf{J}_1, \mathbf{J}_2$ defined in the equations (6) act effectively on their respective space V_1, V_2 and trivially on the other one; that yields the representation of the equations (7). A vector of the 6-dimensional space $V_1 \oplus V_2$ is naturally decomposed in a direct sum that we denote by $\begin{pmatrix} x \\ y \end{pmatrix}$. Moreover $V_1 \oplus V_2$ is an orthogonal space with the scalar product obtained as matrix product:

$$(x' \ y') \begin{pmatrix} x'' \\ y'' \end{pmatrix} = x' \cdot x'' + y' \cdot y''. \quad (63)$$

Each of the 3-dimensional summand subspace is invariant by a $SO(3)$. For the group $SO(4)$, its matrix $g \sim \theta(u_1, u_2)$ [see (61)] is represented by the matrix $A(g)$ (written in 3×3 blocks):

$$A(g) = \begin{pmatrix} \sigma(u_1) & 0 \\ 0 & \sigma(u_2) \end{pmatrix} \quad (64)$$

where σ has been defined in (47). In the preceding section we have shown that $s \in O(4)$ (defined in (56)) corresponds to the permutation of the two 3-dimensional summand spaces (see (57)):

$$A(s) = \begin{pmatrix} 0 & I_3 \\ I_3 & 0 \end{pmatrix}. \quad (65)$$

So the adjoint representation of the group $O(4)$ is irreducible.

Instead to use for the vector space V of the Lie algebra of $O(4)$ the decomposition $V = V_1 \oplus V_2$ corresponding to the operators $\mathbf{J}_1, \mathbf{J}_2$ it is interesting to use the decomposition $V = V_a \oplus V_p$ corresponding to the effective action of the axial vector operator $\mathbf{J}$ and the polar vector operator $\mathbf{K}$. This can be done by the matrix

$$S = \sqrt{\frac{1}{2}} \begin{pmatrix} I_3 & I_3 \\ I_3 & -I_3 \end{pmatrix}. \quad (66)$$

The conjugation by S diagonalize $A(s)$:

$$SA(s)S^{-1} = A'(s) = \begin{pmatrix} I_3 & 0 \\ 0 & -I_3 \end{pmatrix} \quad (67)$$

$$SA(g)S^{-1} = A'(g) = \frac{1}{2} \begin{pmatrix} \sigma(u_1) + \sigma(u_2) & \sigma(u_1) - \sigma(u_2) \\ \sigma(u_1) - \sigma(u_2) & \sigma(u_1) + \sigma(u_2) \end{pmatrix} \quad (68)$$

In this new decomposition we write the component vectors as:

$$\begin{pmatrix} j \\ k \end{pmatrix} = S \begin{pmatrix} x \\ y \end{pmatrix} \text{ i.e. } j = \frac{x+y}{\sqrt{2}}, \quad k = \frac{x-y}{\sqrt{2}} \quad (69)$$

We denote by g^d the matrices of $SO(4)$ which correspond through equation (57) to the pairs $u = u_1 = u_2$.

The matrices $A'(g^d)$ which represent them in the adjoint representation are block diagonal

$$A'(g^d) = \begin{pmatrix} \sigma(u) & 0 \\ 0 & \sigma(u) \end{pmatrix} \quad (70)$$

They are the matrices of $SO(4)$ which commute with $A'(s)$; as (52) shows they form the subgroup $SO(3)^d$ acting effectively on the axes 1,2,3 of the vector representation of $O(4)$ and leaving the axis 4 fix. The orthogonal group $O(3)^d = SO(3)^d \wedge s$ is the orthogonal group of the physical space; it transforms $j \in V_a, k \in V_p$ respectively as axial and polar vectors.

1. Extension of $O(4)$ by including the time reversal

In classical mechanics of point particles, the operation T which leaves fix the position of the particles and reverses their velocity is called time reversal. So T changes also the sign of angular momenta. More generally in physics, T changes the sign of axial vectors (e.g. the magnetic induction) and leaves fix the polar vectors (electric field, Laplace-Runge-Lenz vector, etc) (Wigner, 1959). Wigner has shown that in quantum physics T is represented by an antiunitary operator. T is an exact symmetry of atomic and molecular physics (except for tiny effects induced by weak interaction!) (Sakurai, 1964). We denote by $O(4) \wedge T$ the group generated by $O(4)$ and T ; it is the full approximate dynamical symmetry group for the Rydberg states. The action of T on V , the space of the adjoint representation, is represented by the matrix $-A'(s)$ where $A'(s)$ (generally called P , the parity operator) is defined in (67). Remark that $O(4) \wedge T$ is not the direct product of $O(4)$ by $Z_2(T)$ since T does not commute with the elements of $O(4)$ not in the subgroup $O(3)^d \times Z(-I_4)$ (the last factor is the center of $O(4)$); it is a semidirect product. The image of the adjoint representation of $O(4) \wedge T$ is isomorphic to $O(4)$.

2. The action of $O(4) \wedge T$ on the vector space V of the adjoint representation and on the phase space Σ .

We begin by study the action of $SO(4)$ on V . It is defined by the image $\vartheta[SO(4)] = SO(3) \times SO(3)$ (62) of $SO(4)$ in the adjoint representation. As we have seen in example 1 of Section II A, in the particular case $n = 3$, there are two strata in the action of $O(3)$: the origin with the stabilizer $O(3)$, and the rest of space with stabilizer $O(2)$. There is a unique invariant, the vector norm $x \cdot x \geq 0$ which defines the orbit space; the two strata are defined by $x \cdot x = 0$ and $x \cdot x > 0$. The invariant, the orbit space, and the orbits in V of the index 2 subgroup $SO(3)$ are identical. The corresponding stabilizers are respectively $SO(3) \cap O(2) = SO(2)$, which are index two subgroups of the stabilizers of $O(3)$. Note that the vector

representation of $SO(3)$ coincides with its adjoint representation. The adjoint representation of $SO(3) \times SO(3)$ is the direct sum of two adjoint representations of $SO(3)$.

We obtain the strata on the space $V = V_1 \oplus V_2$ by using the general theorem:

Theorem 3B2. *In a reducible representation of a compact group, the stabilizer of a vector is the intersection of the stabilizers of its components in the irreducible subspaces.*

The two invariants $x \cdot x$ and $y \cdot y$ label the orbits. The orbit space is the semialgebraic domain $x \cdot x \geq 0, y \cdot y \geq 0$. Its inside corresponds to the generic stratum. Its boundary is the union of the 3 strata $x \cdot x > 0 = y \cdot y$, $x \cdot x = 0 < y \cdot y$, and $x \cdot x = 0 = y \cdot y$. The results are given in Table III. To obtain the stabilizers in $SO(4)$ one must take the counter image ϑ^{-1} of those in $SO(3) \times SO(3)$.

The group $O(4) = SO(4) \wedge s$ is generated by $SO(4)$ and s whose action on V is given in (65): it exchanges the vectors x and y . To write the invariants of $O(4)$ (or of its image $SO(3) \uparrow 2$) we use the symmetric and antisymmetric combinations of those of $SO(4)$

$$\kappa \stackrel{\text{def}}{=} x \cdot x + y \cdot y = j \cdot j + k \cdot k, \quad \kappa > 0, \quad (71a)$$

$$\rho \stackrel{\text{def}}{=} x \cdot x - y \cdot y = 2j \cdot k, \quad (71b)$$

$$-\kappa \leq \rho \leq \kappa \leq 0. \quad (71c)$$

(The second form in j, k is obtained from (69).) Since ρ changes of sign by the exchange $x \leftrightarrow y$ the invariants of the $O(4)$ action on V are κ, ρ^2 and the orbit space is defined by restrictions $\kappa \geq 0, \kappa^2 \geq \rho^2 \geq 0$. The inside of the orbit space (obtained by replacing $\geq$ by $>$) corresponds to the generic stratum. The three non generic strata form the boundary. Their equations are respectively $\kappa > 0, \rho^2 = 0$; $\kappa > 0, \kappa^2 = \rho^2 > 0$; and $\kappa = 0 (\Rightarrow \rho^2 = 0)$. The corresponding orbits in the image $SO(3) \uparrow 2$ are $SO(2) \uparrow 2, SO(3) \times SO(2), SO(3) \uparrow 2$.

Since κ and ρ^2 are also T invariant, $O(4) \wedge T$ has same orbits and same orbit space. The corresponding stabilizers [for the image $(SO(3) \uparrow 2) \wedge T$] are given in Table IV where T_s is the product $Ts = sT$.

Taking into account the physical relation (8) we have defined in IID that the phase space of Rydberg problem has the topology $S_2 \times S_2$ and we have denoted it by Σ . In V this phase space is defined by the equations

$$\Sigma \sim S_2 \times S_2 : \quad \kappa = 1, \rho = 0. \quad (72)$$

It is an orbit of $O(4) \wedge T$ [and even of $SO(4)$] belonging to the stratum $\rho^2 = 0$ of stabilizer $(SO(2) \uparrow 2) \wedge T$.

C. Action of $O(3)$, $SO(3)$, $O(3) \wedge T$, $SO(3) \wedge T$, and $SO(3) \wedge T_s$ on Σ ; their strata, orbits and invariants

In the four dimensional space, the subgroup $SO(3)$ leaving invariant the fourth coordinate is characterized in (64) and (68)

TABLE III. Strata of the $SO(4)$ adjoint representation.

stabilizer ^a	invariants	dim.str. ^b	topology ^c
$SO(3) \times SO(3)$	$x \cdot x = 0 = y \cdot y$	0	one point
$SO(2) \times SO(3)$	$x \cdot x > 0 = y \cdot y$	3	S_2
$SO(3) \times SO(2)$	$x \cdot x = 0 < y \cdot y$	3	S_2
$SO(2) \times SO(2)$	$x \cdot x > 0 < y \cdot y$	6	$S_2 \times S_2$

^aWe give the image by ϑ from the stabilizer.

^bdim.str. means dimension of the stratum.

^cThe topological structure of each orbit is given.

TABLE IV. Strata of the $O(4) \wedge T$ and $O(4)$ adjoint representation. Both groups have the same set of strata but their stabilizers are different.

stabilizer ^a	invariants ^b	dim.str. ^c	topology ^d
$(SO(3) \uparrow 2) \wedge T$	$\kappa = 0 = \rho^2$	0	one point
$(SO(2) \times SO(3)) \wedge T_s$	$\kappa^2 = \rho^2 > 0$	3	$2S_2$
$(SO(2) \uparrow 2) \wedge T$	$\kappa^2 \neq \rho^2 = 0$	3	$S_2 \times S_2$
$(SO(2) \times SO(2)) \wedge T_s$	$\kappa^2 - \rho^2 > 0$	6	$2(S_2 \times S_2)$

^aThe image of the stabilizer is given. For the $O(4)$ adjoint representation T or T_s should be omitted.

^b $\kappa \geq 0$ is implicit

^cdim.str. means the dimension of the stratum.

^dThe topological structure of each orbit is given.

$$r \in SO(3) \leftrightarrow u_1 = u_2 \leftrightarrow \leftrightarrow SO(3)^d \subset SO(3) \times SO(3). \quad (73)$$

In (56) we have defined s , the space inversion of $O(3) = SO(3) \times Z_2(s)$. The restriction of the adjoint representation of $O(4)$ to $O(3)$ is reducible. The matrix S reduces this representation (the reduction is given explicitly in section IIIB, see Eqs. (66) - (69)). This reducible representation of $O(3)$ can be noted $1^+ \oplus 1^-$ where $1^\pm$ is respectively the axial and polar vector representation. In our problem, the axial and polar vectors j, k corresponds respectively to the *angular momentum* and the *Runge Lenz vector*. They satisfy the relations (71) which completely characterize the manifold Σ . We need also the new invariant ξ of $SO(3)$ which we define as

$$-1 \leq \xi \stackrel{\text{def}}{=} j \cdot j - k \cdot k \leq 1. \quad (74)$$

The stabilizers of the action of $O(3)$ on Σ are the intersection of $O(3)$ with the stabilizers of $O(4)$ that we have determined in the Table IV. Theorem 3B2 makes also easy the classification of the strata in the action of $O(3)$ on Σ . Indeed the stabilizers in the 3 dimensional subspaces of j and k are respectively $O(3)$ for the null vector, $C_{\infty h}(j)$ for $j \neq 0$ and $C_{\infty v}(k)$ for $k \neq 0$. So for the points of Σ , when both j, k are non zero vectors (they satisfy $j \cdot k = 0$) the stabilizer is $C_s(j)$, the group generated by the reflection through the plane orthogonal to j . Table V summarizes the data on the three strata which appear in the action of $O(3)$ on Σ .

The stabilizers appearing in the action on Σ of the subgroup $SO(3)$ are obtained by taking the intersection

TABLE V. Strata and orbits in the actions of $O(3)$ and $SO(3)$ on Σ . The orbits of shape S_2 are critical.

G	stabilizer	dim. ^a	equation	n.o. ^b	topol. ^c
$O(3)$	$C_{\infty v}(k)$	2	$\xi = -1$	1	S_2
	$C_{\infty h}(j)$	2	$\xi = 1$	1	S_2
	$C_s(j)$	4	$-1 < \xi < 1$	∞	RP^3
$SO(3)$	C_∞	2	$ \xi = 1$	2	S_2
	1	4	$-1 < \xi < 1$	∞	RP^3

^adim. = dimension of the stratum

^bn.o. = number of orbits.

^ctopol. = topological structure of each orbit.

of $SO(3)$ with the stabilizers of the $O(3)$ action. This shows that on Σ the orbits are the same for $O(3)$ and $SO(3)$. However $SO(3)$ orbits form only two strata: the same open dense stratum with trivial symmetry and one stratum with symmetry C_∞ formed by two orbits $\xi = \pm 1$. Any $SO(3)$ -invariant function on Σ is invariant by $O(3)$ (see table V).

It is general theorem of H. Weyl (1939) that the invariants of a direct sum of representations of $SO(n)$ ($n \geq 3$) are made from all distinct scalar products and determinants. Its application to the action of $SO(3)$ on the 6 dimensional space V proves that κ, ξ, ρ form a minimal set of generators of the invariant polynomials since they are algebraically independent. As a scalar product of an axial vector j and a polar vector k , ρ is a pseudo scalar for $O(3)$. For this group, κ, ξ, ρ^2 form an integrity basis. There are no difference on Σ between the $\mathcal{P}^{O(3)}$ and $\mathcal{P}^{SO(3)}$ invariant polynomial ring since $\rho = 0$ (and $\kappa = 1$).

As we explain in Section II B the values of polynomials of an integrity basis label the orbits. So $O(3)$ and $SO(3)$ have the same orbits on Σ . So on V , when $\rho \neq 0$, the $O(3)$ orbits split into two orbits of $SO(3)$ with opposite values of ρ .

Since κ, ξ, ρ are algebraically independent polynomial on the six dimensional space V , the ring of invariant polynomials of $SO(3)$ and $O(3)$ are the polynomial rings

$$\mathcal{P}_6^{SO(3)} = \mathcal{P}[\kappa, \xi, \rho]; \quad (75a)$$

$$\mathcal{P}_6^{O(3)} = \mathcal{P}[\kappa, \xi, \rho^2]. \quad (75b)$$

Table V shows that any function on Σ , invariant under $O(3)$ or $SO(3)$, depends only on the variable ξ defined in (74); indeed this parameter labels completely the orbits (common to $O(3)$ and $SO(3)$). The geometrical representation of the orbifold (which is a 1D-segment) is given in the Appendix A. The Table V also shows that the two orbits defined by $\xi = \pm 1$ are isolated in their strata; therefore they are critical (see Corollary IIB2a): these two orbits are orbits of extrema of any O_3 or $SO(3)$ invariant real function defined on Σ . We give a direct and explicit proof of this property:

Lemma 3C. Any $O(3)$ -invariant function $f(\xi)$ on Σ has at least two orbits of extrema, defined by $\xi = \pm 1$. Indeed, at the point

$$\begin{pmatrix} j \\ k \end{pmatrix} \in R^6, \quad \nabla \xi = 2 \begin{pmatrix} j \\ -k \end{pmatrix}. \quad (76)$$

For a function on Σ , we have to project $\nabla \xi$ on the tangent plane to Σ . Two normal vectors at $\begin{pmatrix} j \\ k \end{pmatrix} \in \Sigma$ are obtained by differentiating the equations $\kappa = 1, \rho = 0$ defining Σ , i.e.

$$v_1 = \begin{pmatrix} \partial \kappa / \partial j \\ \partial \kappa / \partial k \end{pmatrix} = \begin{pmatrix} j \\ k \end{pmatrix}, \quad v_2 = \begin{pmatrix} \partial \rho / \partial j \\ \partial \rho / \partial k \end{pmatrix} = \begin{pmatrix} k \\ j \end{pmatrix}, \quad v_i v_j = \delta_{ij}. \quad (77)$$

The rank one orthogonal projectors on these two vectors are respectively:

$$P_1 = \begin{pmatrix} j \rangle \langle j & j \rangle \langle k \\ k \rangle \langle j & k \rangle \langle k \end{pmatrix}, \quad P_2 = \begin{pmatrix} k \rangle \langle k & k \rangle \langle j \\ j \rangle \langle k & j \rangle \langle j \end{pmatrix}. \quad (78)$$

Since $P_1 P_2 = 0 = P_2 P_1$ the gradient of ξ on the tangent plane at the point $\begin{pmatrix} j \\ k \end{pmatrix} \in \Sigma$ is:

$$\nabla_\Sigma \xi = (I_6 - P_1 - P_2) \nabla \xi = \begin{pmatrix} (1 - \xi)j \\ -(1 + \xi)k \end{pmatrix}. \quad (79)$$

To end the proof of the lemma 3, we simply verify that this vector vanishes for $\xi = 1$ (so $k = 0$) and for $\xi = -1$ (so $j = 0$). Remark that this vector never vanishes on the interval $-1 < \xi < 1$. So the only other orbits of extrema of $f(\xi)$ occur for the values of ξ on this interval, satisfying $f'(\xi) \equiv \frac{df}{d\xi} = 0$.

The extension to the case of three different two dimensional Lie groups including T -dependent symmetry transformations can be easily done because the space of orbits remains the same and the same invariant ξ can be used to distinguish orbits and strata. These groups are $SO(3) \wedge T$, $O(3) \wedge T$, and $SO(3) \wedge T_s$. Special care should be taken only to specify the stabilizers of different strata. They are given in Table VI.

As explained in section III B 1 the action of T on the adjoint space V is represented by $-A'(s)$, so $T_s = sT$ is represented by $-I_6$. Hence T_s leaves κ, ξ, ρ invariant and the orbits and strata of $SO(3) \wedge T_s$ are those of $SO(3)$. Similarly the orbits and strata of $O(3)$, $O(3) \wedge T$, and $SO(3) \wedge T$ are identical. Invariants κ, ξ, ρ^2 characterize orbits unambiguously. So we have

$$\mathcal{P}_6^{SO(3)} = \mathcal{P}_6^{SO(3) \wedge T_s}, \quad (80a)$$

$$\mathcal{P}_6^{O(3)} = \mathcal{P}_6^{O(3) \wedge T} = \mathcal{P}_6^{SO(3) \wedge T}. \quad (80b)$$

n orbit, common to different groups, has different conjugacy classes of stabilisers for each group. The stabilisers on Σ for these five groups are given in two tables V and VI.

D. Invariants of the one dimensional Lie subgroups of $O(3)$ acting on Σ

Up to a conjugation, there are five one dimensional Lie subgroups of $O(3)$ whose traditional notations in molecular physics are:

TABLE VI. Strata and orbits in the actions of $O(3) \wedge T$ and $SO(3) \wedge T$ on Σ . The orbits of shape S_2 are critical.

G	stabilizer	equation
$O(3) \wedge T$	$C_{\infty v}(k) \wedge T$	$\xi = -1$
	$C_{\infty h}(j) \wedge T_s^a$	$\xi = 1$
	$C_s(j) \wedge T_{s'}^b$	$-1 < \xi < 1$
$SO(3) \wedge T$	$C_{\infty} \wedge T$	$\xi = -1$
	$C_{\infty} \wedge T_2^c$	$\xi = 1$
	T_2^d	$-1 < \xi < 1$
$SO(3) \wedge T_s$	$C_{\infty} \wedge T_s$	$ \xi = 1$
	T_s	$-1 < \xi < 1$

^a T_s is the product of time reversal and reflection in plane orthogonal to j .

^bThis group is generated by the reflection in plane orthogonal to the vector j and by the product Ts' of time reversal T and the reflection s' in plane of j and k .

^c T_2 is the product of time reversal T by C_2 rotation around axis orthogonal to vector j .

^d T_2 is the product of time reversal T by C_2 rotation around k vector.

$$C_{\infty}, C_{\infty h}, C_{\infty v}, D_{\infty}, D_{\infty h}. \quad (81)$$

We denote unit vectors by a hat, e.g. $\hat{n}$, and by $C_{\infty}(\hat{n})$ the group of rotations around the axis defined by $\hat{n}$. The stabilizers for the action of these groups on Σ and on the six dimensional space V are the intersections with the stabilizers of $O(3)$. The generic orbits are one dimensional, so we need at least five polynomial invariants to label the orbits on R^6 , the vector space of the $O(4)$ adjoint representation. With the two coordinate vectors j, k and the vector $\hat{n}$ fixing the C_{∞} axis, we can form five scalar products which are five algebraically independent invariant homogeneous polynomial for C_{∞} ; we label them by Greek letters (κ, ξ, ρ have already been defined):

$$\kappa = j \cdot j + k \cdot k, \quad (82a)$$

$$\xi = j \cdot j - k \cdot k, \quad (82b)$$

$$\rho = 2 j \cdot k, \quad (82c)$$

$$\mu = \hat{n} \cdot j, \quad (82d)$$

$$\nu = \hat{n} \cdot k, \quad (82e)$$

the first three and the last two are respectively of degree two, one in the coordinates ¹⁴.

However this is not enough for generating the ring $\mathcal{P}^{C_{\infty}}$ of C_{∞} polynomial invariants and for labeling all the C_{∞} -orbits. Indeed, the Molien function is:

$$M_{C_{\infty}}(\lambda) = \frac{1}{2\pi} \int_0^{2\pi} \frac{d\theta}{(1-\lambda)^2(1-2\lambda \cos \theta + \lambda^2)^2} \quad (83)$$

¹⁴We could have chosen for the direction $\hat{n}$ the third coordinate axis; then $\mu = j_3, \nu = k_3$.

$$= \frac{1+\lambda^2}{(1-\lambda)^2(1-\lambda^2)^3}.$$

The degrees of λ in the five factors of the denominator are equal to the degrees of the five homogeneous polynomials of variables j_i, k_j of (82). But the numerator requires a sixth generator of $\mathcal{P}^{C_{\infty}}$ of degree 2. The square of this invariant should be a polynomial function of six basic invariant polynomials (82). This statement can also be verified geometrically: indeed any set of values satisfying Schwarz inequalities for the scalar products:

$$\rho^2 \leq \kappa^2 - \xi^2, \quad (84a)$$

$$\mu^2 \leq \frac{1}{2}(\kappa + \xi), \quad (84b)$$

$$\nu^2 \leq \frac{1}{2}(\kappa - \xi) \quad (84c)$$

defines two circles= C_{∞} -orbits which can be distinguished by the sign of

$$\sigma = (\hat{n}, j, k) \equiv \hat{n} \cdot (j \times k). \quad (85)$$

Moreover ¹⁵:

$$\begin{aligned} \sigma^2 &= \frac{1}{4}(\kappa^2 - \xi^2) + \rho\mu\nu \\ &- \left(\frac{1}{4}\rho^2 + \frac{\kappa}{2}(\mu^2 + \nu^2) - \frac{1}{2}\xi\mu^2 + \frac{1}{2}\xi\nu^2\right) \geq 0. \end{aligned} \quad (86)$$

So the module of C_{∞} -invariant functions on V , the 6-dimensional vector space of the $O(4)$ adjoint representation may be represented as

$$\mathcal{P}_6^{C_{\infty}} = P[\kappa, \xi, \rho, \mu, \nu] \bullet (1, \sigma). \quad (87)$$

To each point of the five dimensional domain defined by the inequalities (84) and (86) corresponds a unique C_{∞} orbit and conversely: this is the orbit space $V|C_{\infty}$.

The four other one dimensional subgroups have C_{∞} as invariant subgroup. By a simple application of the theorem explained after (13), we can build their orbit spaces from the one of C_{∞} . Let G be any of the three groups $C_{\infty h}, C_{\infty v}, D_{\infty}$. Then G is the union of two C_{∞} cosets: $G = C_{\infty} \cup C_X C_{\infty}$ where C_X denote respectively the reflections C_v, C_h , and C_2 a rotation by π around an axis (in the plane h) orthogonal to the rotation axis of C_{∞} . The action of the quotient group G/C_{∞} on the C_{∞} orbit space can be obtained by computing the action of these three operations C_X on the C_{∞} invariants ρ, μ, ν, σ (the O_3 -invariants κ, ξ are invariants for its five one dimensional subgroups). The result is given in Table VII.

We call pseudo-invariants those which are multiplied by -1 . Their squares are invariants and we will obtain the set of denominator invariants of G by replacing

¹⁵We use the property that the square of the determinant on m m -component vectors $v_{\alpha}, 1 \leq \alpha \leq m$ is the determinant of the matrix of elements $v_{\alpha} \cdot v_{\beta}$.

the pseudo-invariants among ρ, μ, ν by their square. The product of two pseudo-invariants is an invariant which will be a numerator invariant. We can treat similarly the group $D_{\infty h}$ which is made of the four cosets of C_∞ which are in the union of the 3 groups G 's. So its denominator invariants are $\kappa, \xi, \mu^2, \nu^2, \rho^2$. The first 3 lines of Table VII show that the only non trivial numerator invariant is $\nu\sigma$.

The structure we found for the module of the invariant polynomials on V of these four other one dimensional subgroups of $O(3)$, can be compared with their Molien functions. To compute them it is useful to compute the (incomplete) Molien functions M'_G of the C_∞ cosets not containing 1 of the first three groups. We obtain:

$$M'_{C_{\infty v}} = \frac{1}{2\pi} \int_0^{2\pi} \frac{d\theta}{(1-\lambda^2)^3} = \frac{1}{(1-\lambda^2)^3}, \quad (88a)$$

$$M'_{C_{\infty h}} = \frac{1}{2\pi} \int_0^{2\pi} \frac{d\theta}{(1-\lambda^2)((1-\lambda^2)^2 - 4\lambda^2(\cos \theta)^2)} \\ = \frac{1}{(1-\lambda^2)(1-\lambda^4)}, \quad (88b)$$

$$M'_{D_\infty} = \frac{1}{2\pi} \int_0^{2\pi} \frac{d\theta}{(1+\lambda)^2(1-\lambda^2)^2} \\ = \frac{1}{(1+\lambda)^2(1-\lambda^2)^2}. \quad (88c)$$

We can express the complete Molien function for the invariants in terms of these M' :

$$M_{C_{\infty v}} = \frac{1}{2}(M_{C_\infty} + M'_{C_{\infty v}}), \quad (89a)$$

$$M_{C_{\infty h}} = \frac{1}{2}(M_{C_\infty} + M'_{C_{\infty h}}), \quad (89b)$$

$$M_{D_\infty} = \frac{1}{2}(M_{C_\infty} + M'_{D_\infty}), \quad (89c)$$

$$M_{D_{\infty h}} = \frac{1}{4}(M_{C_\infty} + M'_{C_{\infty v}} + M'_{C_{\infty h}} + M'_{D_\infty}). \quad (89d)$$

Then we obtain for the expression of the Molien functions:

$$M_{C_{\infty v}} = \frac{1+\lambda^2+\lambda^3+\lambda^5}{(1-\lambda)(1-\lambda^2)^3(1-\lambda^4)} \quad (= \frac{1+\lambda^3}{(1-\lambda)(1-\lambda^2)^4}), \quad (90a)$$

$$M_{C_{\infty h}} = \frac{1+2\lambda^3+\lambda^4}{(1-\lambda)(1-\lambda^2)^3(1-\lambda^4)}, \quad (90b)$$

$$M_{D_\infty} = \frac{1+\lambda^2+2\lambda^3}{(1-\lambda^2)^5}, \quad (90c)$$

$$M_{D_{\infty h}} = \frac{1+\lambda^3+\lambda^4+\lambda^5}{(1-\lambda^2)^4(1-\lambda^4)}. \quad (90d)$$

We verify again that Molien functions are rational fractions. They agree with the form of the invariant polynomial modules we have found from Table VIII. However for (90a) the form we have used does not correspond to the reduced one (which is given between brackets). The situation is different from the Smoane counter example referred to in section (II B) after equation (25). The reduced form of the $C_{\infty v}$ Molien function does correspond

to a module given in (91b) while the module corresponding to Table VIII is given in (91a):

$$\mathcal{P}_6^{C_{\infty v}} = P[\kappa, \xi, \rho^2, \mu^2, \nu] \bullet (1, \sigma, \rho\mu, \sigma\rho\mu), \quad (91a)$$

$$\mathcal{P}_6^{C_{\infty h}} = P[\kappa, \xi, \sigma, \mu^2, \nu] \bullet (1, \rho\mu). \quad (91b)$$

To prove the equivalence of these two modules we replace σ by its square in the denominator invariants of (91b) and add to the numerator invariants the numerator invariants multiplied by σ ; the two modules have same basis. Equation (86) shows that σ^2 is a function of ρ^2 and of $\kappa, \xi, \mu^2, \nu, \rho\mu$; since the latter are other invariants of (91b), we can replace σ^2 by ρ^2 ; that ends the transformation of (91b) into (91a). We prefer to use the first form because $\rho = 0$ is one of the equations defining the manifold Σ and our future qualitative analysis uses basically G -invariant functions on Σ (defined by $\kappa = 1, \rho = 0$).

Table IX enables us to write explicitly the structure of the five modules of G -invariant functions on Σ :

$$\mathcal{P}_6^{C_\infty} |_\Sigma = P[\xi, \mu, \nu] \bullet (1, \sigma), \quad (92a)$$

$$\mathcal{P}_6^{C_{\infty v}} |_\Sigma = P[\xi, \mu^2, \nu] \bullet (1, \sigma), \quad (92b)$$

$$\mathcal{P}_6^{C_{\infty h}} |_\Sigma = P[\xi, \mu, \nu^2] \bullet (1, \nu\sigma), \quad (92c)$$

$$\mathcal{P}_6^{D_\infty} |_\Sigma = P[\xi, \mu^2, \nu^2] \bullet (1, \mu\nu, \mu\sigma, \nu\sigma) \quad (92d)$$

$$\mathcal{P}_6^{D_{\infty h}} |_\Sigma = P[\xi, \mu^2, \nu^2] \bullet (1, \nu\sigma). \quad (92e)$$

E. One dimensional Lie subgroups of $O(3) \wedge T$ and their invariants

We present here a simple method for determining all one dimensional Lie subgroups of $O(3) \wedge T$ (up to a conjugation) and their ring of invariant polynomials on V . This yields a new proof for the five groups of the preceding section and a study of eleven new subgroups.

The connected component of the identity for *all* one dimensional Lie subgroups of $O(3) \wedge T$ is C_∞ and it is an invariant subgroup of any of them. There is a partial ordering of their conjugacy classes. The maximal one is $D_{\infty h} \wedge T$. It has $2^3 = 8$ connected components.

$$1 \longrightarrow C_\infty \longrightarrow D_{\infty h} \wedge T \xrightarrow{\phi} Z_2^3 \longrightarrow 1 \quad (93)$$

The quotient group Z_2^3 has 16 subgroups, 7 of two elements, 7 of four elements, itself Z_2^3 (8 elements), and the identity (trivial subgroup). The counter image by ϕ^{-1} of these 16 subgroups yields the 16 one dimensional Lie subgroups of $O(3) \wedge T$. Those which have two connected components are the union of two cosets of C_∞ . The one different of C_∞ is of the form gC_∞ . We can take for g the elements

$$v, h, vh = 2h, T, T_v = vT, T_h = hT, T_2 = 2hT, \quad (94)$$

TABLE VII. Action of C_∞ and discret symmetry generators of the group $O(3) \wedge T$ on a set of C_∞ -invariants. κ and ξ are invariant of the total group $O(3) \wedge T$. They are omitted from the table. The $-$ sign indicates the multiplication by -1 .

element	ρ	μ	ν	σ
C_∞^a	+	+	+	+
C_v	-	-	+	+
C_h	-	+	-	-
C_2	+	-	-	-
T	-	-	+	-
T_v	+	+	+	-
T_h	+	-	-	+
T_2	-	+	-	+

^aThis line is introduced to show explicitly that we deal with invariants of C_∞ group.

where v, h are respectively reflections in a plane containing the C_∞ axis and in a plane perpendicular to it. (We could have taken, instead of h , the space inversion $i = h2_v$. We follow the tradition of molecular physicists which prefer the notation $C_{\infty h}$ to $C_{\infty i}$.) The corresponding notation for these seven groups with two connected components is

$$\begin{aligned} &C_{\infty v}, C_{\infty h}, D_\infty, \\ &C_\infty \wedge T, C_\infty \wedge T_v, C_\infty \wedge T_h, C_\infty \wedge T_2. \end{aligned} \quad (95)$$

We have seen that κ, ξ are denominator invariants of $O(3)$ and they are also T invariant. So they are denominator invariants for all 16 subgroups we study in this subsection. The action of the seven elements of (94) (or of the seven groups of (95) on the C_∞ invariants ρ, μ, ν, σ is easy to study. We can determine the action of the three operations v, h, T . These operations generate the quotient group Z_2^3 , so they yield the action of all other elements of these groups. This action is given in Table VII. From it we obtain easily the modules of invariant polynomials. They are given in the second part of Table IX.

Table VIII give the structure of the seven groups with 4 connected components ($= 4$ cosets) of C_∞ . Then from Table VII we obtain the action of these groups on the C_∞ invariants ρ, μ, ν, σ . Remark that each column of Table VII has exactly four $+$ signs. So the polynomial heading this column is invariant for only one 4-component group. These groups are different and therefore the three other invariants are squares. To find other numerator invariants of these groups one has to find sets of columns for which the product of signs is $+$ in the three lines corresponding to each of these seven groups. The method extends to $D_{\infty h} \wedge T$ by requiring the same result for all the lines. The results are given in third and fourth parts of the Table IX.

The restriction of the system of invariant polynomials on Σ becomes especially simple for four symmetry groups $C_\infty \wedge T_v, C_{\infty v} \wedge T, C_{\infty h} \wedge T_2$, and $D_{\infty h} \wedge T$. For all these groups we have on Σ only three denominator invariants.

TABLE VIII. Description of one dimensional subgroups of $O(3) \wedge T$ with four connected components in terms of continuous and discret symmetry elements. Sign $+$ means that the corresponding element belong to the symmetry group.

C_∞	C_v	C_h	C_2	T	T_v	T_h	T_2	Group ^a
+	+	+	+					$D_{\infty h}$
+	+			+	+			$C_{\infty v} \wedge T$
+		+		+		+		$C_{\infty h} \wedge T$
+			+	+			+	$D_\infty \wedge T$
+	+					+	+	$C_{\infty v} \wedge T_h$
+		+			+		+	$C_{\infty h} \wedge T_v$
+			+		+	+		$D_\infty \wedge T_v$
+	+	+	+	+	+	+	+	$D_{\infty h} \wedge T$

^aAlternative notation for $C_{\infty v} \wedge T$ is $C_{\infty v} \wedge T_2$, for $C_{\infty h} \wedge T_v$ is $C_{\infty h} \wedge T_2$, for $D_\infty \wedge T_v$ is $D_\infty \wedge T_h$, and for $D_{\infty h} \wedge T$ is $D_{\infty h} \wedge T_\alpha$ with $T_\alpha = T_v, T_h$, or T_2 .

TABLE IX. Denominator and numerator invariants in the action on R^6 of the 16 one dimensional Lie subgroups of $O(3) \wedge T$. $\theta_1 = \kappa$ and $\theta_2 = \xi$ are present for all subgroups and therefore omitted from the table. Invariants which have a fixed value on $\Sigma \equiv S_2 \times S_2$ (due to $\rho = 0$) are between $()$. Four parts of the Table correspond respectively to connected subgroup C_∞ , to seven subgroups with two connected components, to seven subgroups with four connected components and to $D_{\infty h} \wedge T$ group with eight connected components.

G	θ_3	θ_4	θ_5	φ_1	φ_2	φ_3
C_∞	(ρ)	μ	ν	σ		
$C_{\infty v}$	(ρ^2)	μ^2	ν	σ	$(\rho\mu)$	$(\rho\mu\sigma)$
$C_{\infty h}$	(ρ^2)	μ	ν^2	$\nu\sigma$	$(\rho\nu)$	$(\rho\sigma)$
D_∞	(ρ)	μ^2	ν^2	$\mu\nu$	$\mu\sigma$	$\nu\sigma$
$C_\infty \wedge T$	(ρ^2)	μ^2	ν	$\mu\sigma$	$(\rho\mu)$	$(\rho\sigma)$
$C_\infty \wedge T_v$	(ρ)	μ	ν			
$C_\infty \wedge T_h$	(ρ)	μ^2	ν^2	σ	$\mu\nu$	$(\mu\nu\sigma)$
$C_\infty \wedge T_2$	(ρ^2)	μ	ν^2	σ	$(\nu\rho)$	$(\nu\rho\sigma)$
$D_{\infty h}$	(ρ^2)	μ^2	ν^2	$\nu\sigma$	$(\mu\rho\sigma)$	$(\mu\nu\rho)$
$C_{\infty v} \wedge T$	(ρ^2)	μ^2	ν	$(\mu\rho)$		
$C_{\infty h} \wedge T$	(ρ^2)	μ^2	ν^2	$\mu\nu\sigma$	$(\sigma\rho)$	$(\mu\nu\rho)$
$D_\infty \wedge T$	(ρ^2)	μ^2	ν^2	$\mu\sigma$	$(\nu\mu\rho)$	$(\nu\sigma\rho)$
$C_{\infty v} \wedge T_h$	(ρ^2)	μ^2	ν^2	σ	$(\nu\mu\rho)$	$(\nu\mu\sigma\rho)$
$C_{\infty h} \wedge T_v$	(ρ^2)	μ	ν^2	$(\nu\rho)$		
$D_\infty \wedge T_v$	(ρ)	μ^2	ν^2	$\mu\nu$		
$D_{\infty h} \wedge T$	(ρ^2)	μ^2	ν^2	$(\rho\mu\nu)$		

$$\mathcal{P}_6^{C_\infty \wedge T_v}|_\Sigma = P[\xi, \mu, \nu], \quad (96a)$$

$$\mathcal{P}_6^{C_\infty \wedge T}|_\Sigma = P[\xi, \mu^2, \nu], \quad (96b)$$

$$\mathcal{P}_6^{C_\infty \wedge T_2}|_\Sigma = P[\xi, \mu, \nu^2], \quad (96c)$$

$$\mathcal{P}_6^{D_\infty \wedge T}|_\Sigma = P[\xi, \mu^2, \nu^2]. \quad (96d)$$

It is curious to note that especially these groups have the most natural physical interpretation.

$C_\infty \wedge T$ is the symmetry group for the atom in static electric field or for rydberg states of heteronuclear diatomic molecule.

$C_\infty \wedge T_v$ is the symmetry group of an atom in constant magnetic field (Zeeman effect).

$C_\infty \wedge T_v$ is the maximal common subgroup of $C_\infty \wedge T$ and $C_\infty \wedge T_v$. Thus it corresponds to the symmetry of atom under the simultaneous presence of two parallel magnetic and electric fields.

$D_\infty \wedge T$ group is the symmetry group for rydberg states of homonuclear diatomic molecule, or of the quadratic Zeeman effect.

F. Orbits, strata and orbit spaces of one dimensional Lie subgroups of $O(3)$ acting on Σ

The stabilizers of $O(3)$ have been determined in Table V; they belong to three $O(3)$ conjugation classes: those of $C_\infty(k)$, $C_\infty(j)$, $C_s(j)$. The stabilizers of the five groups G of (81) are their intersection with the stabilizers of $O(3)$. So, for these group G , we can directly make the list of strata, and give the invariant equations (for closed strata) and/or inequalities which define them. We are interested only about the orbits and strata on Σ . These informations are given in table X below.

First, let us write again all equations on the C_∞ invariants when they are restricted on the manifold Σ defined by $\kappa = 1$ and $\rho = 0$. This corresponds to the study of the three dimensional orbifold $\Sigma|C_\infty$. Equations (84), (86) become:

$$\mu^2 \leq \frac{1}{2}(1 + \xi), \quad (97a)$$

$$\nu^2 \leq \frac{1}{2}(1 - \xi), \quad (97b)$$

$$-\frac{1}{2} \leq \sigma \leq \frac{1}{2} \quad (97c)$$

and

$$0 \leq 4\sigma^2 = (1 - \xi^2) - 2(1 - \xi)\mu^2 - 2(1 + \xi)\nu^2 \leq 1. \quad (98)$$

This last equation shows explicitly that σ is determined up to a sign by ξ, μ^2, ν^2 . From the two previous equations we deduce:

$$\mu = \pm 1 \Rightarrow \xi = 1, \nu = 0 = \sigma, \quad (99a)$$

$$\nu = \pm 1 \Rightarrow \xi = -1, \mu = 0 = \sigma. \quad (99b)$$

This means that for a given $\hat{n}$ there are four points A, B, C, D of Σ fixed by $C_\infty(\hat{n})$:

$$A : j = \hat{n}, k = 0, \quad (100a)$$

$$\equiv \mu = 1, \xi = 1, \nu = 0;$$

$$B : j = -\hat{n}, k = 0, \quad (100b)$$

$$\equiv \mu = -1, \xi = 1, \nu = 0,$$

$$C : k = \hat{n}, j = 0, \quad (100c)$$

$$\equiv \nu = 1, \xi = -1, \mu = 0,$$

$$D : j = 0, k = -\hat{n}, \quad (100d)$$

$$\equiv \nu = -1, \xi = -1, \mu = 0.$$

On $S_2 \times S_2$ the four points correspond to the pairs of poles: NN, SS, NS, SN respectively. As we shall see any function invariant by one of the five one dimensional Lie subgroups of $O(3)$, has an extremum on each of these four points of Σ .

Similarly, we have two circles on Σ :

$$\Gamma_1 : k = 0, n \cdot j = 0 \Rightarrow \xi = 1, \mu = \nu = 0, \quad (101a)$$

$$\Gamma_2 : j = 0, n \cdot k = 0 \Rightarrow \xi = -1, \mu = \nu = 0. \quad (101b)$$

They correspond, on the two equators of $S_2 \times S_2$, to pairs of identical points, diametrically opposed points, respectively. Each of these two circles Γ_1, Γ_2 form a critical orbit of D_∞ or $D_{\infty h}$.

Finally, theorem cited in III B 2 advises us to consider the particular cases where one of the vectors j, k vanishes, i.e. $\xi = \pm 1$. When $\xi = 1$ then $k = 0$; since any axial vector j is invariant by the symmetry through the origin (while any non trivial polar vector changes of sign), $\xi = 1$ contains a stratum with stabilizer C_i (the group generated by the symmetry through the origin) for the groups $C_\infty h$ and $D_\infty h$. When $\xi = -1$ then $j = 0$ and the polar vector k is invariant by the symmetry through any plane containing it. The symmetry through the plane which contains also $\hat{n}$ belongs to a stabilizer of $C_\infty v$ and $D_\infty h$ and this is still true when $j \neq 0$ and collinear to $\hat{n} \times k$. See table X.

The five orbit spaces $\Sigma|G$, are of dimension three.¹⁶ We will first make a direct study of their topology. We shall first prove that topologically $\Sigma|C_\infty \sim S_3$. Then, as suggested by the $-$ signs in the columns of μ, ν, σ of table VII, the orbit spaces of $C_\infty v$, $C_\infty h$, D_∞ are obtained by identifying the points symmetrical through respectively, a 3,2,1 dimensional linear manifold containing the center of the sphere S_3 .

¹⁶Some general results are known on the topology of 3-manifolds (a short for three-dimensional manifolds): (Fomenko, 1983; Thurston, 1969). They may be used to find the topology of the orbifolds on the basis of the geometrical representation (see Appendix A).

TABLE X. Strata and orbits in the action of the five one dimensional Lie subgroups of $O(3)$ on Σ .

G^a ΣG	Stabilizer ^b	gc ^c	dim. ^d strat.	strata equations ^e and inequalities	number ^f orbits	nature ^g orbits	cr? ^h
C_∞	C_∞	c	0	$\mu^2 = 1, \nu^2 = 1$	4	A, B, C, D	cr
S_3	1	g	4	$\mu^2 < 1, \nu^2 < 1$	∞^3	S_1	
$C_{\infty v}$	$C_{\infty v}$	c	0	$\nu^2 = 1$	2	C, D	cr
	C_∞	c	0	$\mu^2 = 1$	1	AB	cr
B_3	$C_s(j')$		3	$\mu = 0, \nu^2 < 1$	∞^2	S_1	
	1	g	4	$0 < \mu^2 < 1 \Rightarrow \nu^2 < 1$	∞^3	$2S_1$	
$C_{\infty h}$	$C_{\infty h}$	c	0	$\mu^2 = 1$	2	A, B	cr
	C_∞	c	0	$\nu^2 = 1$	1	CD	cr
S_3	$C_s(n)$		2	$0 \leq \frac{1+\xi}{2} = \mu^2 < 1 \Rightarrow \nu = 0$	∞	S_1	
	C_i		2	$\xi = 1, \mu^2 < 1$	∞	S_1	
	1	g	4	$\xi < 1, 0 < \mu^2 < 1 \Rightarrow \nu^2 < 1$	∞^3	$2S_1$	
D_∞	C_∞	c	0	$\mu^2 + \nu^2 = 1, \mu\nu = 0$	2	AB, CD	cr
$Susp.$	C_2	c	1	$\xi^2 = 1, \mu = \nu = 0$	2	Γ_1, Γ_2	cr
RP^2	1	g	4	$(\xi^2 = 1, 0 < \mu^2 < 1, 0 < \nu^2 < 1)$	∞^3	$2S_1$	
$D_{\infty h}$	$C_{\infty h}$	c	0	$\mu^2 = 1$	1	AB	cr
	$C_{\infty v}$	c	0	$\nu^2 = 1$	1	CD	cr
	$C_{2h}(j)$	c	1	$\xi = 1, \mu = \nu = 0$	1	Γ_1	cr
	$C_{2v}(k)$	c	1	$\xi = -1, \mu = \nu = 0$	1	Γ_2	cr
B_3	$C_s(n)$		2	$0 \leq \frac{1+\xi}{2} = \mu^2 < 1 \Rightarrow \nu = 0$	∞	$2S_1$	
	C_i		2	$\xi = 1, 0 < \mu^2 < 1$	∞	$2S_1$	
	$C_s(j')$		3	$\mu = 0, \nu^2 < 1, \xi < 1 + \nu^2$	∞^2	$2S_1$	
	1	g	4	$0 < \mu^2 < \frac{1+\xi}{2} < 1, \nu^2 < \frac{1-\xi}{2} < 1,$ $(\xi - 1)^2 + \mu^2 + \nu^2 > 0$	∞^3	$4S_1$	

^aColumn 1: below the group G is given the topological nature of the orbit space $\Sigma|G$ (Susp. is for suspension).

^bColumn 2: stabilizer of the stratum. $C_s(j') = C_s(j)$ except when $j = 0$; then it is $C_s(\hat{n} \times k)$.

^cColumn 3: c is for closed stratum and g for generic stratum.

^dColumn 4: dimension of the stratum.

^eColumn 5: the stratum is a semi-algebraic set; its defining polynomial equations and inequalities are given here.

^fColumn 6: number of orbits in the stratum.

^gColumn 7: geometry of each orbit in the stratum.

^hColumn 8: critical orbits have a "cr" in this column.

In the 4-dimensional space of parameters ξ, μ, ν, σ , when $-1 < \xi < 1$, equation (98) shows that the section of $\Sigma|C_\infty \sim S_3$ by a hyper-plane $\xi = \text{constant}$ is an ellipsoid $\sim S_2$:

$$\begin{aligned} -1 < \xi < 1, \\ 2\sigma^2 + (1 - \xi)\mu^2 + (1 + \xi)\nu^2 &= \frac{1}{2}(1 - \xi^2). \end{aligned} \quad (102)$$

Indeed this is true because each coefficient (function of ξ) is strictly positive. Furthermore this equation implies (97). We are left to study the particular two cases: $\xi = \pm 1$.

$$\xi = 1 \Rightarrow \nu = \sigma = 0 \quad (103)$$

and from (97a) : $-1 \leq \mu \leq 1$. Similarly

$$\xi = -1 \Rightarrow \mu = \sigma = 0 \quad (104)$$

and from (97b): $-1 \leq \nu \leq 1$. These two segments of line are the limits when $\xi \rightarrow \pm 1$ of the ellipsoids defined by (102). This proves that the orbifold for the C_∞ action on Σ is the 3D-sphere

$$\Sigma|C_\infty \sim S_3 \quad (105)$$

with four marked points. Its four points A, B, C, D represent four critical orbits of one point each, and the complement is the image of the generic stratum. Remark that in the invariant space of "orthogonal coordinates" σ, ξ, μ, ν , the orbit space $\Sigma|C_\infty$ has three symmetry hyper-planes $\sigma = 0, \mu = 0, \nu = 0$, mutually orthogonal.

The table IX shows that $\Sigma|C_{\infty v}$ is obtained from $\Sigma|C_\infty$ by identifying its points of coordinates $\xi, \sigma, \nu, \pm\mu$. We can represent it by the intersection of $\Sigma|C_{\infty v}$ with the closed half-space $\mu \geq 0$. This orbit space $\Sigma|C_{\infty v}$ is therefore topologically equivalent to a hemisphere, i.e. a ball B_3 .

$$\Sigma|C_\infty \cap (\mu \geq 0) = \Sigma|C_{\infty v} \sim B_3. \quad (106)$$

This is also the topological nature of the projection of $\Sigma|C_{\infty v}$ on its symmetry hyper-plane $\mu = 0$; indeed from $(1 - \xi)\mu^2 \geq 0$ we deduce from the equation (98) that

$$2\sigma^2 + \frac{1}{2}\xi^2 + (1 + \xi)\nu^2 \leq \frac{1}{2}; \quad (107)$$

but one must remark that there is a unique point of this projection which does not correspond to a unique point of the orbit space $\Sigma|C_{\infty v}$: indeed $\xi = 1, \sigma = \mu = \nu = 0$ if the projection of the whole segment $\xi = 1, \sigma = \nu = 0, -1 \leq \mu \leq 1$. To summarize, table X shows that the orbit space $\Sigma|C_{\infty v}$ contains four strata represented by:

1. 2 points C, D defined in (100d, 100e): each corresponds to a one point $C_{\infty v}$ -orbit;
2. 1 point $X : \xi = 1 = \mu, \sigma = 0 = \nu$, representing an two point C_∞ -orbit, $\{A, B\}$ (see (100b, 100c));

3. The boundary ($\partial B_3 \sim S_2$) minus the two points C, D representing the C_s stratum;
4. The interior of B_3 minus the point X representing the generic stratum.

We now prove $\Sigma|C_{\infty h} \sim S_3$. Indeed, from table IX in the parameter space one obtain $\Sigma|C_{\infty h}$ from $\Sigma|C_\infty$ by identifying the points symmetrical through the 2-plane $\mathcal{P}(\xi, \mu)$ of the coordinates ξ, μ (it is the intersection of the two symmetry hyper-planes $\nu = 0, \sigma = 0$). Consider the sphere $S_3: \xi^2 + \mu^2 + \nu^2 + \sigma^2 = 1$ topologically equivalent to $\Sigma|C_\infty$. By identification of its points in the pair $s_\pm = (\xi, \mu, \pm\nu, \pm\sigma)$ (which are not in $\mathcal{P}(\xi, \mu)$), one obtains a topological space $\sim \Sigma|C_{\infty h}$. The projection on the 2-plane $\mathcal{P}(\xi, \mu)$ is the disk $B_2 : \xi^2 + \mu^2 \leq 1$. Note that $\partial B_2 = S_3 \cap \mathcal{P}(\xi, \mu)$ while each point $p(\xi, \mu)$ of the interior of B_2 is the projection of a circle Γ_p of equation $\nu^2 + \sigma^2 = 1 - \xi^2 - \mu^2$ in the 2-plane perpendicular to $\mathcal{P}(\xi, \mu)$. By the identification of its points symmetric through its center the circle Γ_p is transformed into a circle Γ'_p ; this is for each p in the interior of B_2 . Correspondingly this point identification transforms S_3 into S'_3 .

We note from table IX that one transforms $\Sigma|C_{\infty h}$ into $\Sigma|D_{\infty h}$ by identifying the points of opposite μ coordinate. As for the transformation of $\Sigma|C_\infty$ into $\Sigma|C_{\infty v}$ study above we obtain that $\Sigma|D_{\infty h} \sim B_3$.

We are left with the study of $\Sigma|D_\infty$. It is obtained from $\Sigma|C_\infty$ by identifying the points in each pair $s_\pm = (\xi, \pm\mu, \pm\nu, \pm\sigma)$ i.e. the points symmetric through the axis intersection of the three symmetry hyper-planes $\mu = 0, \nu = 0, \sigma = 0$. This axis is the normal to the hyper-plane $\mathcal{H}: \xi = 0$. We remark that $\Sigma|C_\infty \sim S_3$ is topologically equivalent to the double cone of vertices $\pm 1, 0, 0, 0$ and basis $\Upsilon = (\Sigma|C_\infty) \cap \mathcal{H} \sim S_2$; this is also called a suspension of Υ . The point identification identifies the points of Υ symmetrical though its center and transforms it into $\Upsilon' \sim RP^2$. So:

$$\Sigma|D_\infty \sim \text{suspension}(RP^2). \quad (108)$$

Table X gives in its first column the topological nature of the five orbit spaces studied in this section. The geometrical representation of the orbit spaces for one dimensional Lie subgroups studied in this section is discussed in more detail in the Appendix A.

G. Invariants of finite subgroups of $O(3)$ acting on Σ

The construction of invariant functions on the Σ manifold is based on the preliminary construction of the integrity basis on the 6 dimensional space where the action of the symmetry group of the problem is linear. The Molien function and the invariants themselves for the 6 dimensional space $x+y$ or $k+j$ may be found from known expressions for Molien functions and integrity bases for irreducible representations. Next step includes the restriction of the polynomial algebra on the sub-manifold

Σ of the 6D-space. The general procedure of the restriction of the polynomial ring defined on the manifold to the sub-manifold was outlined in sub-subsection II B 1. The submanifold Σ is defined in the 6 dimensional space $x+y$ by the polynomial equations $x^2 = 1/2$, $y^2 = 1/2$. If the point symmetry group does not include improper rotations (inversion or reflections) these polynomials may always be considered as denominator invariants. In such a case we just eliminate them from the integrity basis constructed for the 6D-space and the resulting integrity basis gives the basis for the 4D submanifold.

For point groups which are not the subgroups of $SO(3)$ we start with the consideration of the similar problem for the proper rotation subgroup and after that take into account the effect of improper symmetry elements working directly on the 4D-submanifold Σ .

The detailed realization of this procedure is given in the Appendix B on several examples. Below we just summarize the results for the case of the C_2 point group as the invariance group of the problem.

Let take x_3 and y_3 to coincide with the C_2 axis. In such a case x_1, x_2, y_1, y_2 transform according to the B representation and x_3, y_3 according to the A representation of the C_2 point group. We are interested in the module of invariant functions defined on the submanifold Σ given by two polynomial equations

$$x_1^2 + x_2^2 + x_3^2 = 1/2, \quad (109a)$$

$$y_1^2 + y_2^2 + y_3^2 = 1/2 \quad (109b)$$

After the restriction on Σ the Molien function for invariants has the form

$$M_{C_2}|_{\Sigma} = \frac{1+6\lambda^2+\lambda^4}{(1-\lambda^2)^2(1-\lambda)^2}. \quad (110)$$

The explicit form of the module of invariant functions on Σ may be easily given as well:

$$\mathcal{P}^{C_2}|_{\Sigma} = P[x_1^2, x_3, y_1^2, y_3] \bullet (1, \varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6, \varphi_7), \quad (111)$$

where

$$\varphi_1 = x_1 y_1, \varphi_2 = x_2 y_1, \varphi_3 = x_1 y_2, \varphi_4 = x_2 y_2, \quad (112)$$

$$\varphi_5 = x_1 x_2, \varphi_6 = y_1 y_2, \varphi_7 = x_1 x_2 y_1 y_2. \quad (113)$$

More condensed notation for the set of numerator invariants may be used

$$\mathcal{P}^{C_2}|_{\Sigma} = P[x_1^2, x_3, y_1^2, y_3] \bullet ((1, x_1 x_2)(1, y_1 y_2), (x_1, x_2)(y_1, y_2)). \quad (114)$$

Instead of listing explicitly (as in (111)) all eight numerator invariants, we show in (114) that they may be reconstructed as products of slightly simpler monomials. One should remark that the choice of denominator and numerator invariants is not unique and that proposed here is just one of possible. Much more information may be found in the Appendix B.

TABLE XI. Strata and orbits in the action of C_{2v} on Σ .

Stabilizer	gc ^a	dim. ^b	number ^c	nature ^d
C_{2v}	c	0	2	1
C_2	c	0	1	2
C_s^v		2	∞^2	2
C_s^d		2	∞^2	2
1	g	4	∞^4	4

^ag is for generic stratum; c is for closed stratum.

^bDimension of the stratum.

^cNumber of orbits in the stratum. ∞^n stands for n -dimensional stratum.

^dNumber of points in each orbit.

H. Orbits, strata and orbit spaces of finite subgroups of $O(3)$ acting on Σ

The strata for any finite subgroup G of $O(3)$ for its 6 dimensional representation ($k+j$ which is the sum of polar and axial vector representations) follow immediately from the well known results for polar and axial vector representations. We list below strata for group actions on Σ manifold for several point groups which are the most interesting from the point of view of possible applications. These are examples of molecules with the C_{2v} , D_{3h} , and T_d point symmetry. Similar tables for all other possible group symmetries are given in the Appendix C. The Tables listed in this subsection show in column 1 the stabilizer of the stratum. In column 2 closed and generic strata are indicated. We remark once more that some strata are neither closed nor generic. In column 3 the dimension of the stratum is given. For the finite group action on Σ the dimension of the generic stratum is always 4. Column 4 gives the number of orbits in the stratum. If the dimension of the stratum is zero the number of orbits in the stratum is finite. If the dimension of the stratum is positive the number of orbits in the stratum is infinite. We mark it ∞^n with n equal the dimension of the stratum. Column 5 shows the number of points in each orbit. For finite group actions on Σ this number is always finite and for the generic stratum it is equal to the number of elements of group.

I. Orbits, strata, and orbit spaces for T -dependent subgroups of $O(3) \wedge T$.

We have shown that there are 16 one-dimensional Lie subgroups of the complete symmetry group $O(3) \wedge T$ of the problem. There is naturally many finite subgroups which can be obtained in a way similar to our construction of one dimensional subgroups. Extension of point subgroups of $O(3)$ to points subgroups of $O(3) \wedge T$ is analogous in some sense to construction of antisymmetry (Shubnikov, 1951) or magnetic symmetry groups (color groups) well known in solid state physics (Hamermesh, 1964; Shubnikov and Belov, 1964).

TABLE XII. Strata and orbits in the action of D_{3h} on Σ .

Stabilizer	gc ^a	dim. ^b	number ^c	nature ^d
C_{3h}	c	0	1	2
C_{3v}	c	0	1	2
C_{2v}	c	0	2	3
C_2	c	0	1	6
C_{1h}		2	∞^2	6
C_s		2	∞^2	6
1	g	4	∞^4	12

^ag is for generic stratum; c is for closed stratum.^bDimension of the stratum.^cNumber of orbits in the stratum. ∞^n stands for n -dimensional stratum.^dNumber of points in each orbit.TABLE XIII. Strata and orbits in the action of T_d on Σ .

Stabilizer	gc ^a	dim. ^b	number ^c	nature ^d
C_{3v}	c	0	2	4
C_3	c	0	1	8
S_4	c	0	1	6
C_{2v}	c	0	1	6
C_s		2	∞^2	12
1	g	4	∞^4	24

^ag is for generic stratum; c is for closed stratum.^bDimension of the stratum.^cNumber of orbits in the stratum. ∞^n stands for n -dimensional stratum.^dNumber of points in each orbit.

We give below the analysis of the orbits, strata and orbit spaces for some of groups including time reversal. We have chosen those groups which have simple physical realization as symmetry groups of the hydrogen atom under presence of different external fields. This simple quantum system enables one to study quite a lot of different invariance symmetry groups.

Let us consider several physical situations together with more or less detailed description of corresponding symmetry groups.

- Hydrogen atom without any external fields. The symmetry group includes the full orthogonal group

TABLE XIV. Invariant manifolds for $C_{\infty h} \wedge T_v$ symmetry group action on Σ . (Hydrogen atom in magnetic field.)

Stabilizer	Dim	Equations
$C_{\infty h} \wedge T_v$	0	$\mu = \pm 1$
$C_{\infty} \wedge T_v$	0	$\nu^2 = 1$
$[C_h \times T_v]^a$	2	$\nu^2 = 0; \xi = 2\mu^2 - 1$
$[C_i \times T_v]^b$	2	$\nu^2 = 0; \xi = 1$
T_v	3	$\sigma = 0$
T_2	3	$\nu^2 = 0$
C_1	4	Σ

^aThis group includes four elements: E, σ_h, T_v, T_2 .^bThis group includes four elements: E, i - inversion, T_v, T_2 .

$O(3)$ and the time reversal. We can write the group as the direct product $O(3) \wedge T$ where $T = \{E, T\}$ is the two element group $Z_2(T)$ formed by identity E and time reversal T . In fact, the dynamic symmetry group for hydrogen atom in the absence of external fields is higher. We use this higher group to introduce the approximate quantum number corresponding to an individual n -shell of the Rydberg atom even in the case of external fields (assuming that the splitting of the n -shell is small as compared to the inter- n -shell gap). Different external fields break this symmetry till various subgroups.

- Hydrogen atom under the presence of constant magnetic field. This case corresponds to the Zeeman effect for the hydrogen atom. $C_{\infty h}$ group is the invariance group of spatial geometric transformations. The complete symmetry group including time reversal operations is $C_{\infty h} \wedge T_v$. It is the semi direct product of $C_{\infty h}$ and two element group $T_v = \{E, T_v\}$ including two elements: the identity E and the product of time reversal and space reflection T_v in the plane of symmetry axis. The group $C_{\infty h} \wedge T_v$ includes following classes of conjugated elements: $\{E\}$ - identity, $\{\sigma_h\}$ - reflection in the plane orthogonal to the magnetic field axis, $\{R_\phi\}$ - rotation on angle ϕ around magnetic field, $\{S_\phi\}$ - rotation-reflection on angle ϕ around magnetic field, $\{T_v(\phi)\}$ - time reversal followed by reflection in a plane passing through the magnetic field, $\{T_2(\phi)\}$ - product of time reversal and rotation by π around an axis orthogonal to the field axis. An operation T_2 can be equivalently described as product of T_v and S_ϕ operations. Table XIV gives the invariant manifolds for the $C_{\infty h} \wedge T_v$ group action on Σ . We give here invariant manifolds instead of strata to simplify the defining equations.
- Hydrogen atom under the presence of constant electric field. This is the case of the Stark effect for the hydrogen atom. $C_{\infty v}$ group is the invariance group of spatial geometric transformations. The invariance under the time reversal takes place under the absence of magnetic field as well. Therefore the complete invariance group can be written as $C_{\infty v} \times T$. This group includes following symmetry operations: E - identity, T - time reversal, R_ϕ - rotation on angle ϕ around electric field, σ_ϕ - reflection in plane passing through the field axis, TR_ϕ - time reversal followed by rotation, $T_s(\phi)$ - time reversal followed by reflection. System of invariant manifolds of the $C_{\infty v} \times T$ action on Σ is given in Table XVI.
- Collinear electric and magnetic fields. The symmetry group includes C_{∞} subgroup of rotations around the common direction of the electric and magnetic field. The complete invariance group can be written as $C_{\infty} \wedge T_v$. Naturally, this group is

TABLE XV. Invariant manifolds for $C_\infty \wedge T_v$ symmetry group action on Σ . (Hydrogen atom in parallel magnetic and electric fields.)

Stabilizer	Dim	Equations
$C_\infty \wedge T_v$	0	$\nu^2 = 1; \mu^2 = 1$
T_v	3	$\sigma = 0$
C_1	4	Σ

the subgroup of the symmetry group appropriate for the case of only electric or only magnetic field. System of invariant manifolds of the $C_\infty \wedge T_v$ action on Σ is given in Table XV.

- Orthogonal electric and magnetic fields. The symmetry group is finite in this case and includes only four symmetry elements: identity E , reflection in the plane orthogonal to the magnetic field σ_h , product $T\sigma_v$ of time reversal T and reflection σ_v in plane formed by two orthogonal fields, and the symmetry operation TC_2 which is the product of the time reversal T and the C_2 rotation around the electric field direction. We will use the notation G_4 for this symmetry group. This group has three subgroups of order two which will be useful below. The group T_v includes as nontrivial symmetry operation the product $T\sigma_v$ of time reversal T and reflection σ_v in plane formed by two orthogonal fields. The group C_s includes the reflection in the plane orthogonal to the magnetic field (this plane includes the electric field vector). The group T_2 includes as nontrivial symmetry operation the product of time reversal and the C_2 rotation around the electric field direction.
- Generic nonorthogonal non-collinear configuration of two fields. The symmetry group T_s has order two and includes one nontrivial symmetry operation $T\sigma$ which is the product of the time reversal and the reflection in plane formed by two fields. T_s is the subgroup of the symmetry group G_4 for orthogonal fields and the subgroup of the symmetry group $C_{\infty v} \wedge T_s$ for collinear fields. It is the only common subgroup for these two important limiting cases of parallel and orthogonal fields.
- To complete the list of interesting symmetry groups we add here the symmetry group of the quadratic Zeeman effect or of Rydberg states of homonuclear diatomic molecule. This is the $D_{\infty h} \times T$ group which is the maximal onedimensional subgroup of the $O(3) \wedge T$ symmetry group. The set of invariant manifolds for this group is given in the Table XVII.

Inclusion of additional symmetry operation enables us to simplify in such physically important cases as the Zeeman effect, Stark effect, hydrogen atom in parallel fields or quadratic Zeeman effect the integrity basis and the geometrical representation of the orbifold. Going from

TABLE XVI. Invariant manifolds for $C_{\infty v} \times T$ symmetry group action on Σ . (Hydrogen atom in electric field.)

Stabilizer	Dim	Equations
$C_{\infty v} \times T$	0	$\nu = \pm 1$
$C_\infty \wedge T_v$	0	$\mu^2 = 1$
$[C_s \times T_{sr}]^a$	2	$\mu^2 = 0; \xi = 1 - 2\nu^2$
$[C_s \times T]$	2	$\mu^2 = 0; \xi = -1$
C_s	3	$\mu^2 = 0$
T_v	3	$\sigma = 0$
C_1	4	Σ

^aThis group includes four elements: E - identity, σ - reflection in the plane including field axis and orthogonal to the vector $\mathbf{L}$, T_{sr} - time reversal followed by reflection in the plane formed by field axis and vector $\mathbf{L}$, T_2 - time reversal followed by rotation over π around field axis.

TABLE XVII. Invariant manifolds for $D_{\infty h} \wedge T$ symmetry group action on Σ . (Complete symmetry group of the quadratic Zeeman effect.)

Stabilizer	Dim	Equations
$C_{\infty h} \wedge T_s$	0	$\mu^2 = 1$
$C_{\infty v} \wedge T$	0	$\nu^2 = 1$
$C_{2h} \wedge T_s^a$	1	$\xi = 1, \mu^2 = \nu^2 = 0$
$C_{2v} \wedge T$	1	$\xi = -1, \mu^2 = \nu^2 = 0$
$C_s(n) \wedge T_s^b$	2	$1 + \xi = 2\mu^2$
$C_i \wedge T_s$	2	$\xi = 1$
$C_s(j) \wedge T_2^c$	3	$\mu^2 = 0$
T_s	3	$\sigma^2 = 0$
C_1	4	Σ

^a C_{2h} subgroup includes symmetry plane orthogonal to the vector $\mathbf{L}$; T_s is the time reversal followed by reflection in plane formed by $\mathbf{L}$ and magnetic field.

^b C_s is the reflection in plane orthogonal to C_∞ axis; T_s is the time reversal followed by reflection in plane of $\mathbf{K}$ and $\mathbf{L}$.

^c T_2 is the time reversal followed by C_2 rotation around $\mathbf{K}$.

FIG. 12. Space of orbits for the $C_{\infty h} \wedge T_s$ action on Σ . (H atom under the presence of magnetic field.)

FIG. 13. Space of orbits for the $C_{\infty} \wedge T_s$ action on Σ . (H atom under the presence of parallel magnetic and electric fields.)

the C_{∞} to $C_{\infty} \wedge T_s$, from $C_{\infty v}$ to $C_{\infty v} \wedge T$, from $C_{\infty h}$ to $C_{\infty h} \wedge T_s$, and from $D_{\infty h}$ to $D_{\infty h} \wedge T$ leads to integrity basis consisting of only basic "denominator" invariants. Space of orbits for extended groups possesses more rich stratification (see Tables XV, XVI, XIV, XVII) but the geometrical form of the orbifold becomes simpler (see Figs. 13, 14, 12) as compared to the geometrical form of the orbifold for purely geometrical point symmetry group studied in the Appendix A.

Similar extension of geometrical point symmetry group can be done in cases of finite symmetry groups; e.g. example of the G_4 symmetry group for the hydrogen atom in two orthogonal fields mentioned shortly earlier in this section is analyzed in more details in section V D and in a separate publication (Sadovskii and Zhilinskii, 1997).

FIG. 14. Space of orbits for the $C_{\infty v} \wedge T$ action on Σ . (H atom under the presence of electric field.)

IV. CONSTRUCTION AND ANALYSIS OF RYDBERG HAMILTONIANS.

A. Effective Hamiltonians

Let discuss now the simplest effective Hamiltonians invariant with respect to subgroups of the $O(4)$ group and their relation with invariant functions defined on Σ manifold. We start with the Hamiltonian for a hydrogen atom which is $O(4)$ invariant

$$H = \frac{1}{2\mu} p^2 - \frac{1}{r}; \quad E_n = -\frac{1}{2n^2}. \quad (115)$$

Due to the specific Coulomb interaction there are two vector integrals of motion: $\mathbf{J}$ - the angular momentum vector, and $\mathbf{X}$ - the Laplace-Runge-Lenz vector,

$$\mathbf{X} = \mathbf{p} \times \mathbf{J} - \frac{\mathbf{r}}{r}. \quad (116)$$

After the energy dependent scaled transformation

$$\mathbf{K} = \mathbf{X}(-2E_n)^{-1/2} \quad (117)$$

$\mathbf{J}$ and $\mathbf{K}$ form the $o(4)$ Lie algebra with defining commutation relations

$$[J_\alpha, J_\beta] = i\varepsilon_{\alpha\beta\gamma} J_\gamma, \quad (118a)$$

$$[J_\alpha, K_\beta] = i\varepsilon_{\alpha\beta\gamma} K_\gamma, \quad (118b)$$

$$[K_\alpha, K_\beta] = i\varepsilon_{\alpha\beta\gamma} J_\gamma, \quad (118c)$$

and two important relations

$$\mathbf{J}^2 + \mathbf{K}^2 = n^2 - 1; \quad (119a)$$

$$(\mathbf{J} \cdot \mathbf{K}) = 0. \quad (119b)$$

If we consider a slightly perturbed Hamiltonian which conserves essentially the presence on n multiplets typical

for hydrogen atom (this is precisely the situation with Rydberg atoms and molecules in the limit of small splitting of n multiplets) an effective Hamiltonian for a given n shell may be written as a phenomenological effective Hamiltonian constructed from $\mathbf{J}$ and $\mathbf{K}$ operators. The relations (119) are important to reach the correspondence between the quantum operators $\mathbf{J}$ and $\mathbf{K}$ satisfying relations (119) and its classical analogs, because the classical variables j, k satisfy the normalization condition (71), (72) which is independent on the particular realization of the quantum operator for any concrete n shell. As a consequence the correspondence between quantum operators and classical dynamic variables has the form

$$J_\alpha \leftrightarrow \sqrt{n^2 - 1} j_\alpha, \quad (120a)$$

$$K_\alpha \leftrightarrow \sqrt{n^2 - 1} k_\alpha \quad (120b)$$

Using the integrity basis for the classical representation we can construct now easily the basic polynomial invariants formed by quantum operators and to indicate their classical analogs

$$J^2 - K^2 = (n^2 - 1) \xi, \quad (121a)$$

$$J_z = \sqrt{n^2 - 1} \mu, \quad (121b)$$

$$K_z = \sqrt{n^2 - 1} \nu. \quad (121c)$$

For higher order invariants one needs to make the anti-symmetrization of the operators which do not commute. For example, the operators representing the auxiliary numerator invariants have the form

$$\{J_x, K_y\} - \{J_y, K_x\} = (n^2 - 1) \sigma, \quad (122a)$$

$$\{K_z, (\{J_x, K_y\} - \{J_y, K_x\})\} = \quad (122b)$$

$$= (n^2 - 1)^{3/2} \nu \sigma,$$

$$\{J_z, K_z\} = (n^2 - 1) \mu \nu \quad (122c)$$

$$\{J_z, (\{J_x, K_y\} - \{J_y, K_x\})\} = \quad (122d)$$

$$= (n^2 - 1)^{3/2} \mu \sigma.$$

where

$$\{A, B\} = \frac{1}{2}(AB + BA). \quad (123)$$

Sometimes it is useful to work in the x, y representation (71) instead of j, k . We denote corresponding quantum operators by

$$\mathbf{J}_1 = (\mathbf{J} - \mathbf{K})/2; \quad (124a)$$

$$\mathbf{J}_2 = (\mathbf{J} + \mathbf{K})/2. \quad (124b)$$

The Hilbert space of wave-functions associated with the n multiplet may in such a case be formed by the basis

$$|J_1 = J_2 = (n - 1)/2; M_1, M_2\rangle, \quad (125a)$$

$$M_i = -(n - 1)/2, \dots, (n - 1)/2. \quad (125b)$$

The correspondence between quantum operators $\mathbf{J}_1, \mathbf{J}_2$ and classical dynamic variables follows directly from (121, 122)

$$\mathbf{J}_1 \cdot \mathbf{J}_2 = (n^2 - 1) \xi/4; \quad (126a)$$

$$J_{1z} + J_{2z} = 2\sqrt{n^2 - 1} \mu; \quad (126b)$$

$$J_{1z} - J_{2z} = \sqrt{n^2 - 1} \nu, \quad (126c)$$

$$J_{1y}J_{2x} - J_{1x}J_{2y} = (n^2 - 1) \sigma/2, \quad (126d)$$

$$\{(J_{1z} - J_{2z}), (J_{1y}J_{2x} - J_{1x}J_{2y})\} = \quad (126e)$$

$$= (n^2 - 1)^{3/2} \nu \sigma,$$

$$J_{1z}^2 - J_{2z}^2 = (n^2 - 1) \mu \nu, \quad (126f)$$

$$\{(J_{1z} + J_{2z}), (J_{1y}J_{2x} - J_{1x}J_{2y})\} = \quad (126g)$$

$$= (n^2 - 1)^{3/2} \mu \sigma.$$

There are two ways leading to the construction of the effective operators. One is a purely phenomenological approach based on the utilization of all operators allowed by symmetry with their coefficients being the adjustable parameters of the model. Another uses the transformation of the initially complete operator to the effective one by applying some kind of perturbation theory or contact transformation etc. This second procedure results in the effective operator with fixed coefficients which depend on the initial complete Hamiltonian. Both approaches result in the Hamiltonian which may be written in terms of integrity basis. We recall that as soon as invariant polynomials are known an arbitrary Hamiltonian may be written in the form of expansion (properly symmetrized to take into account the non-commutativity of quantum operators) in terms of denominator invariants θ_i and numerator invariants φ_s

$$H = \sum_{n_1, n_2, \dots, n_k}^{\infty} \sum_s C_{n_1, n_2, \dots, n_k; s} \varphi_s \theta_1^{n_1} \theta_2^{n_2} \dots \theta_k^{n_k} \quad (127)$$

Explicit form of invariants for all continuous subgroups of $O(3)$ was found in subsection III D (see Table IX) and for some point groups in subsection III G and in Appendix B. Purely phenomenological way to represent effective Hamiltonians supposes that all $C_{n_1, n_2, \dots, n_k; s}$ coefficients are adjustable parameters, whereas perturbation treatment gives $C_{n_1, n_2, \dots, n_k; s}$ coefficients in (127) as explicit functions of the parameters of the initial complete Hamiltonian.

We will start by analyzing first the phenomenological approach to the construction of effective Hamiltonians taking into account their symmetry properties. The main idea of our approach is to introduce along with the phenomenological construction some kind of complexity classification of effective Hamiltonians which is based on the quantitative measure - the number of orbits of extrema. We also call them the stationary orbits (points or finite number of points or manifolds).

B. Qualitative description of effective Hamiltonians invariant with respect to continuous subgroups of $O(3)$

We discuss here the qualitative classification of effective Hamiltonians invariant with respect to different symmetry groups. By qualitatively different Hamiltonians we mean those operators which are characterized by different sets of stationary orbits with each stationary orbit characterizing by its stabilizer and Morse index.

The number of stationary orbits may be used as a measure of the complexity of the Hamiltonian. The zero level of complexity corresponds to a set of Hamiltonians with the minimal possible number of stationary orbits (compatible with the topological structure and the symmetry group action according to equivariant Morse-Bott theory). We will list below qualitatively different Morse-Bott Hamiltonians of some low level of complexity, whereas in the Appendix D more general results are outlined.

1. $O(3)$ invariant Hamiltonian

Any $O(3)$ invariant Hamiltonian may be written in the form

$$H = H(\xi), \quad (128)$$

where $H(\xi)$ is an arbitrary (sufficiently good) function of one variable which is defined for $-1 \leq \xi \leq 1$. ξ is the only invariant polynomial which is not constant on the Σ manifold (see subsection III C). For quantum operators instead of ξ we should use equivalent operator given by (121a) (or (126a)) in J, K (or J_1, J_2) representation. So any effective Hamiltonian may be written as a power series in ξ or more generally as an arbitrary function of ξ as in (128).

Any $O(3)$ invariant classical Hamiltonian possesses two critical manifolds due to the presence of two critical orbits. These two critical orbits have very simple physical meaning. $C_{\infty h}$ critical orbit corresponds on the orbifold to the point $\xi = 1$ ($j \cdot j = 1, k \cdot k = 0$) i.e. the quantum state localized near this point has maximal (possible for a given n) value of the orbital momentum $\ell = n - 1$. Another critical orbit corresponds to the point $\xi = -1 \sim (j \cdot j = 0, k \cdot k = 1)$ i.e. for the quantum problem the quantum state localized in the phase space near this point possesses minimal possible value of the orbital momentum $\ell = 0$.

More complicated Hamiltonians can be classified according to number of stationary orbits (which are the RP^3 manifolds) situated on the generic C_s stratum. Qualitatively different generic $O(3)$ invariant Hamiltonians are given in the Table XVIII.

It is clear that any $O(3)$ invariant Hamiltonian results in a system of energy levels which is completely characterized by one quantum number ℓ , the weight of the

TABLE XVIII. Classification of qualitatively different $O(3)$ invariant Hamiltonians due to the complexity level.

Level of complexity ^b	$C_{\infty v}$ stratum	$C_{\infty h}$ stratum	N_{st} ^a with index 0	N_{st} with index 1
0	max	min	no	no
0	min	max	no	no
1	max	max	no	1
1	min	min	1	no
2	max	min	1	1
2	min	max	1	1
$2p$	max	min	p	p
$2p$	min	max	p	p
$2p+1$	max	max	p	$p+1$
$2p+1$	min	min	$p+1$	p

^a N_{st} is the number of stationary RP^3 manifolds on C_s stratum.

^b p is nonnegative integer.

irreducible representation of the group $O(3)$. This one regular sequence may be rather complicated in general case but for the simplest Morse Bott type Hamiltonian ($p = 0$ in Table XVIII) the sequence should be monotonic. It is reasonable to assume that the number of extrema of the $H = H(\xi)$ function in a general case is much smaller than the number n limiting possible ℓ values. In such a case the energy spectrum explicitly shows the regular behavior. In contrast, if the number of extrema on $H(\xi)$ is larger or of the same order than n (assuming n is large), the energy spectrum may seem to be erratic.

Near extremum, corresponding to the $C_{\infty h}$ critical orbit ($\xi = 1 \sim (j \cdot j = 1, k \cdot k = 0)$) for any (sufficiently good) Hamiltonian there is a system of regular energy levels,

$$E(\ell) = \text{const } \ell(\ell + 1) \quad (129)$$

characterizing by $\ell = (n - 1), (n - 2), \dots$, whereas near extremum, corresponding to the $C_{\infty v}$ critical orbit ($\xi = -1 \sim (j \cdot j = 0, k \cdot k = 1)$) there is a regular system of energy levels,

$$E(\ell) = \text{const } \ell(\ell + 1) \quad (130)$$

which is characterized by $\ell = 0, 1, 2, \dots$. Near an extremum corresponding to generic C_s orbit the system of energy levels may be described as a bent series of the form

$$E(\ell) = \text{const } [\ell(\ell + 1) - \ell_0(\ell_0 + 1)]^2 \quad (131)$$

with the ℓ value varies around some generally non-integer ℓ_0 value.

2. C_∞ invariant Hamiltonian

The C_∞ invariant phenomenological Hamiltonian may be written as

TABLE XIX. Classification of qualitatively different C_∞ invariant Hamiltonians.

Level of complexity ^c	C_∞^a stratum	C_1^b stratum
$0^\pm$	$1 + 2t^2 + t^4$	<i>no</i>
1	$1 + 3t^2$	t^3
1	$1 + t^2 + 2t^4$	t^2
$2^\pm$	$1 + 2t^2 + t^4$	$t + t^2$
2	$1 + 2t^2 + t^4$	$1 + t$
$2^\pm$	$4t^2$	$1 + t^3$
$2^\pm$	$2 + 2t^4$	$t + t^2$
2	$1 + 3t^4$	$2t^2$
2	$2 + 2t^2$	$t + t^3$

^aMorse counting polynomial is given in this column to characterize the system of stationary orbits.

^bMorse counting polynomial for the S_1 stationary orbits is given.

^cThe super index $\pm$ in the first column indicates those classes which are invariant under the sign inversion of the Hamiltonian.

$$H_{C_\infty} = \sum C_{n_1, n_2, n_3} \xi^{n_1} \mu^{n_2} \nu^{n_3} \quad (132)$$

$$+ \sum C_{n_1, n_2, n_3; \sigma} \sigma \xi^{n_1} \mu^{n_2} \nu^{n_3}$$

with ξ, μ, ν, σ given in (121, 122a, 126) with all necessary symmetrization. Any Hamiltonian (132) has four critical orbits (stationary points A, B, C, D , see Table X and (103)). There is only one type of the simplest C_∞ invariant Hamiltonian. It is characterized by the absence of critical manifolds of nonzero dimension. (See Table XIX). The simplest classical Hamiltonian possesses one minimum and one maximum on two critical orbits and two saddle points (with Morse index 2) on another pairs of critical orbits. The description of qualitatively different Hamiltonians of the 1 and 2 level of complexity is given in the Table XIX as well.

We use in the Table XIX Morse counting polynomials to represent the system of stationary orbits for a given set of the qualitatively similar Hamiltonians. To reduce the number of different classes we neglect in the Table XIX all Hamiltonians which may be obtained by a simple transformation (H) $\leftrightarrow$ ($-H$). It is clear that the inversion of the sign of the Hamiltonian is associated with the transformation of the Morse indices of stationary points ($k \leftrightarrow (4 - k)$) and of one-dimensional stationary manifolds ($k \leftrightarrow (3 - k)$). For several classes both Hamiltonians H and ($-H$) are described by the same Morse counting polynomial (we add to the level of complexity the index $\pm$ in such a case, see Table XIX) For all other classes the change of the sign of the Hamiltonian will modify the redistribution of the stationary orbits over Morse indices. For example, there are two extra classes of the Hamiltonians of the 1 level of complexity and three additional classes for the second level of complexity, but we omit them from the Table.

Near minimum and maximum the simplest Morse type C_∞ -invariant Hamiltonian (zero level of complexity) may

FIG. 15. Qualitative energy level pattern for effective C_∞ -invariant Hamiltonian of the simplest Morse-Bott type. In the neighborhood above the minimum and below the maximum the energy level pattern is similar to that of two-dimensional isotropic harmonic oscillator.

be approximated as 2D-isotropic harmonic oscillator. So it is characterized by a qualitative energy level pattern shown in Fig.15. Lower and upper parts of the multiplet are formed by a sequence of polyads typical for 2D-isotropic harmonic oscillator.

3. $C_{\infty v}$ invariant Hamiltonian

The $C_{\infty v}$ invariant phenomenological Hamiltonian may be written as

$$H_{C_{\infty v}} = \sum C_{n_1, n_2, n_3} \xi^{n_1} (\mu^2)^{n_2} \nu^{n_3} \quad (133)$$

$$+ \sum C_{n_1, n_2, n_3; \sigma} \sigma \xi^{n_1} (\mu^2)^{n_2} \nu^{n_3}$$

with $\xi, (\mu^2), \nu$ as denominator invariants and σ as one numerator invariant given in (121, 122a, 126) with all necessary symmetrization. Any Hamiltonian (133) has three critical orbits: one C_∞ orbit consisting of two stationary points (A, B) and two $C_{\infty v}$ orbits consisting of one stationary point (C, D) each (stationary points A, B, C, D , see Table X and (103)).

The most natural physical application of $C_{\infty v}$ symmetry concerns the Stark effect. In this case the symmetry group should be extended to include the time reversal as a symmetry operation. Taking into account the invariance of ξ, μ^2, ν with respect to time reversal and the alternation of the sign of σ under the same operation the general form of the Hamiltonian (133) becomes simpler. In the case of Stark effect the effective Hamiltonian (133) is independent on σ .

4. $C_{\infty h}$ invariant Hamiltonian

The $C_{\infty h}$ invariant phenomenological Hamiltonian may be written as

$$H_{C_{\infty h}} = \sum C_{n_1, n_2, n_3} \xi^{n_1} \mu^{n_2} (\nu^2)^{n_3} + \sum C_{n_1, n_2, n_3; \nu \sigma} (\nu \sigma) \xi^{n_1} \mu^{n_2} (\nu^2)^{n_3} \quad (134)$$

with $\xi, \mu, (\nu^2)$ as denominator invariants and $(\nu \sigma)$ as one numerator invariant as given in (121, 122b, 126) with all necessary symmetrization. Any Hamiltonian (134) has three critical orbits: one C_{∞} orbit consisting of two stationary points (C, D) and two $C_{\infty h}$ orbits consisting of one stationary point (A, B) each (stationary points A, B, C, D , see Table X and (103)).

In the case of Zeeman effect after extending the symmetry group from $C_{\infty h}$ till $C_{\infty h} \wedge T_s$ (see Sec. III I) the general form of the effective Hamiltonian becomes independent on $(\nu \sigma)$.

5. D_{∞} invariant Hamiltonian

The D_{∞} invariant phenomenological Hamiltonian may be written as

$$H_{D_{\infty}} = \sum C_{n_1, n_2, n_3} \xi^{n_1} (\mu^2)^{n_2} (\nu^2)^{n_3} + \sum C_{n_1, n_2, n_3; \nu \sigma} (\nu \sigma) \xi^{n_1} (\mu^2)^{n_2} (\nu^2)^{n_3} + \sum C_{n_1, n_2, n_3; \mu \sigma} (\mu \sigma) \xi^{n_1} (\mu^2)^{n_2} (\nu^2)^{n_3} + \sum C_{n_1, n_2, n_3; \nu \mu} (\nu \mu) \xi^{n_1} (\mu^2)^{n_2} (\nu^2)^{n_3} \quad (135)$$

with $\xi, (\mu^2), (\nu^2)$ as denominator invariants and $(\nu \sigma), (\mu \sigma)$, and $(\nu \mu)$ as three numerator invariants as given in (121, 122, 126) with all necessary symmetrization. Any Hamiltonian (135) has four critical orbits: two C_{∞} orbit consisting each of two stationary points (A, B) and (C, D) and two C_2 orbits (both being S_1 stationary manifold Γ_1, Γ_2) (stationary points A, B, C, D , and stationary circles Γ_1, Γ_2 see Table X and (103, 104)).

6. $D_{\infty h}$ invariant Hamiltonian

The $D_{\infty h}$ invariant phenomenological Hamiltonian may be written as

$$H_{D_{\infty h}} = \sum C_{n_1, n_2, n_3} \xi^{n_1} (\mu^2)^{n_2} (\nu^2)^{n_3} + \sum C_{n_1, n_2, n_3; \nu \sigma} (\nu \sigma) \xi^{n_1} (\mu^2)^{n_2} (\nu^2)^{n_3} \quad (136)$$

with $\xi, (\mu^2), (\nu^2)$ as denominator invariants and $(\nu \sigma)$ as one numerator invariant as given in (121, 122b, 126) with all necessary symmetrization. Any Hamiltonian (136) has four critical orbits: one $C_{\infty h}$ orbit consisting of two

stationary points (A, B) , one $C_{\infty v}$ orbit consisting of two stationary points (C, D) , one C_{2h} orbit consisting of S_1 stationary manifold Γ_1 , and one C_{2v} orbit consisting of S_1 stationary manifold Γ_2 , (stationary points A, B, C, D , and stationary circles Γ_1, Γ_2 see Table X and (103, 104)).

C. Qualitative description of effective Hamiltonians invariant with respect to finite subgroups of $O(3)$

We characterize below in Tables XX, XXI the simplest Morse type functions for all finite point symmetry groups. For finite groups orbits include a finite number of isolated point and any Morse type function possesses only isolated extrema. We can work within the initial Morse theory (without extension to Morse-Bott approach). For each point group the possible sets of stationary points are indicated up to trivial change of Morse indices $c_k \leftrightarrow c_{4-k}$. Stationary points for each group are split into columns according to their Morse index k . The number of stationary points c_k with the Morse index k within each orbit and their symmetry types are given. If there are several orbits of stationary points with the same Morse index it is indicated explicitly as a sum. It should be noted that for many point groups the stationary points are situated on zero dimensional strata only and their positions are fixed (i.e. only critical orbits are present) (see subsection III H and Appendix C for the description of all strata for the finite group action on Σ). For some low symmetry groups (C_1, C_s, S_2) there are no orbits isolated within the stratum and the positions of stationary points are not fixed by symmetry. At the same time the presence of closed 2D-stratum for C_s and S_2 groups indicates that a number of stationary points should lie on the closed stratum. For these groups it is necessary to verify further Morse inequalities for the restriction of the complete initial function on the closed stratum.

For O_h and I_h groups only part of simplest Morse functions is given in Table XXI. To obtain the complete list it is necessary to interchange in all possible manner C_{nv} and C_{nh} critical orbits.

Near minima or maxima any Hamiltonian may be approximately represented as 2D-harmonic oscillator. Taking into account the presence of several, say k , (k is the dimension of the orbit of stationary points) equivalent by symmetry minima the model problem appropriate for the description of internal dynamics near the extrema is the motion of a particle in a 2D-potential with k equivalent extrema (the potential can be anisotropic or isotropic and slightly anharmonic near each extremum) assuming small tunneling between different extrema. We can introduce three characteristic parameters for such a problem: i) anisotropy of the 2D-harmonic oscillator, ii) anharmonicity of the 2D-oscillator, and iii) splitting due to tunneling.

Let consider several simple limiting situations from the point of view of the energy level patterns for quantum

TABLE XX. Simplest Morse type functions defined on Σ manifold under the presence of point symmetry group (lower symmetry groups).

Point group	c_0 (c_4)	c_1 (c_3)	c_2	c_3 (c_1)	c_4 (c_0)
C_1	$1(C_1)$	<i>no</i>	$2(C_1)$	<i>no</i>	$1(C_1)$
C_s	$1(C_s)$	<i>no</i>	$2(C_1)$	<i>no</i>	$1(C_s)$
	$1(C_s)$	<i>no</i>	$1(C_s)+1(C_s)$	<i>no</i>	$1(C_s)$
S_2	$1(S_2)$	<i>no</i>	$2(C_1)$	<i>no</i>	$1(S_2)$
	$1(S_2)$	<i>no</i>	$1(S_2)+1(S_2)$	<i>no</i>	$1(S_2)$
S_{2n} $n \geq 2$	$1(S_{2n})$	<i>no</i>	$2(C_n)$	<i>no</i>	$1(S_{2n})$
C_n $n \geq 2$	$1(C_n)$	<i>no</i>	$1(C_n)+1(C_n)$	<i>no</i>	$1(C_n)$
C_{nh} $n \geq 2$	$1(C_{nh})$	<i>no</i>	$2(C_n)$	<i>no</i>	$1(C_{nh})$
C_{nv} $n \geq 2$	$1(C_{nv})$	<i>no</i>	$2(C_n)$	<i>no</i>	$1(C_{nv})$
D_2 ^a	$2(C_2)$	$2C_2$	$2(C_2)+2(C_2)$	$2(C_2)$	$2(C_2)$
D_n ^b $n \geq 3$	$2(C_n)$	$n(C_2)$	$n(C_2)+n(C_2)$	$n(C_2)$	$2(C_n)$
	$2(C_n)$	$n(C_2)$	$n(C_2)+2(C_n)$	$n(C_2)$	$n(C_2)$
	$n(C_2)$	$n(C_2)$	$2(C_n)+2(C_n)$	$n(C_2)$	$n(C_2)$
$n = 3, 5$ only	$2(C_n)+2(C_n)$	$n(C_2)$	$n(C_2)$	$n(C_2)$	$n(C_2)$
D_{nh} (D_{nd}) $n \geq 3$, odd	$2(C_{nh})$	$n(C_{2v})$	$2n(C_2)$	$n(C_{2v})$	$2(C_{nv})$
D_{nh} (D_{nd}) $n \geq 2$, even	$2(C_{nh})$	$n(C_{2h})$	$n(C_{2v})+n(C_{2h})$	$n(C_{2v})$	$2(C_{nv})$
	$2(C_{nh})$	$n(C_{2h})$	$n(C_{2v})+n(C_{2v})$	$n(C_{2h})$	$2(C_{nv})$
	$2(C_{nh})$	$n(C_{2v})$	$n(C_{2v})+n(C_{2h})$	$n(C_{2h})$	$2(C_{nv})$
	$2(C_{nh})$	$n(C_{2v})$	$n(C_{2h})+n(C_{2h})$	$n(C_{2v})$	$2(C_{nv})$
$n = 4$ only	$2(C_{4h})+2(C_{4v})$	$4(C_{2v})$	$4(C_{2h})$	$4(C_{2v})$	$4(C_{2h})$
$n = 4$ only	$2(C_{4h})+2(C_{4v})$	$4(C_{2v})$	$4(C_{2h})$	$4(C_{2h})$	$4(C_{2v})$
$n = 4$ only	$2(C_{4h})+2(C_{4v})$	$4(C_{2v})$	$4(C_{2v})$	$4(C_{2h})$	$4(C_{2h})$
$n = 4$ only	$2(C_{4h})+2(C_{4v})$	$4(C_{2h})$	$4(C_{2h})$	$4(C_{2v})$	$4(C_{2v})$
$n = 4$ only	$2(C_{4h})+2(C_{4v})$	$4(C_{2h})$	$4(C_{2v})$	$4(C_{2v})$	$4(C_{2h})$
$n = 4$ only	$2(C_{4h})+2(C_{4v})$	$4(C_{2h})$	$4(C_{2v})$	$4(C_{2h})$	$4(C_{2v})$

^aThere are three different C_2 strata for the D_2 group. Each stratum includes two orbits. To reach complete description of qualitatively different Morse type function it is necessary to precise the stratum for all stationary points.

^bThere are two different C_2 strata for even $n \geq 4$, whereas there is only one stratum for odd n .

^cFurther specification of strata is needed. There are three different C_{2v} and three different C_{2h} strata for the D_{2h} (D_{2d}) group. There are two different C_{2v} and two different C_{2h} strata for the D_{nh} (D_{nd}) group for $n \geq 4$, even.

TABLE XXI. Simplest Morse type functions defined on Σ manifold under the presence of point symmetry group (higher symmetry groups).

Point group	c_0 (C_4)	c_1 (C_3)	c_2	c_3 (C_1)	c_4 (C_0)
T	$4(C_3)$	$6(C_2)$	$4(C_3)+4(C_3)$	$6(C_2)$	$4(C_3)$
T_h	$4(C_{3h})$	$6(C_{2h})$	$8(C_3)$	$6(C_{2v})$	$4(C_{3h})$
T_d	$4(C_{3v})$	$6(S_4)$	$8(C_3)$	$6(C_{2v})$	$4(C_{3v})$
O	$6(C_4)$	$12(C_2)$	$6(C_4)+8(C_3)$	$12(C_2)$	$8(C_3)$
	$6(C_4)$	$12(C_2)$	$8(C_3)+8(C_3)$	$12(C_2)$	$6(C_4)$
	$8(C_3)$	$12(C_2)$	$6(C_4)+6(C_4)$	$12(C_2)$	$8(C_3)$
	$6(C_4)+6(C_4)$	$12(C_2)$	$8(C_3)$	$12(C_2)$	$8(C_3)$
O_h (^a)	$6(C_{4h})$	$12(C_{2h})$	$6(C_{4v})+8(C_{3h})$	$12(C_{2v})$	$8(C_{3v})$
	$6(C_{4h})$	$12(C_{2h})$	$8(C_{3h})+8(C_{3v})$	$12(C_{2v})$	$6(C_{4v})$
	$8(C_{3h})$	$12(C_{2h})$	$6(C_{4h})+6(C_{4v})$	$12(C_{2v})$	$8(C_{3v})$
	$6(C_{4h})+6(C_{4v})$	$12(C_{2h})$	$8(C_{3h})$	$12(C_{2v})$	$8(C_{3v})$
I	$12(C_5)$	$30(C_2)$	$12(C_5)+20(C_3)$	$30(C_2)$	$20(C_3)$
	$12(C_5)$	$30(C_2)$	$20(C_3)+20(C_3)$	$30(C_2)$	$12(C_4)$
	$20(C_3)$	$30(C_2)$	$12(C_5)+12(C_5)$	$30(C_5)$	$20(C_3)$
	$12(C_5)+12(C_5)$	$30(C_2)$	$20(C_3)$	$30(C_2)$	$20(C_3)$
I_h (^a)	$12(C_{5h})$	$30(C_{2h})$	$12(C_{5v})+20(C_{3h})$	$30(C_{2v})$	$20(C_{3v})$
	$12(C_{5h})$	$30(C_{2h})$	$20(C_{3h})+20(C_{3v})$	$30(C_{2v})$	$12(C_{5v})$
	$20(C_{3h})$	$30(C_{2h})$	$12(C_{5h})+12(C_{5v})$	$30(C_{2v})$	$20(C_{3v})$
	$12(C_{5h})+12(C_{5v})$	$30(C_{2h})$	$20(C_{3h})$	$30(C_{2v})$	$20(C_{3v})$

^aTo complete the list of Morse functions it is necessary to add other sets of stationary points resulting from different permutations within pairs of C_{nv} and C_{nh} strata.

problem near extrema. Let δ^{ani} be the anisotropy of the model Hamiltonian near extremum

$$\delta^{ani} \sim h|\nu_1 - \nu_2|/(\nu_1 + \nu_2), \quad (137)$$

where ν_i are two harmonic frequencies of the model operator, δ^{tun} be the characteristic energy splitting due to tunneling, and δ^{anh} be the anharmonicity correction.

In some cases the harmonic approximation of the Hamiltonian near extremal orbit should be isotropic due to symmetry (extremal orbit is a critical one with its stabilizer being group with high symmetry). In such a case we have only anharmonicity parameter δ^{anh} and the tunneling splitting parameter δ^{tun} . Typically δ^{anh} is sufficiently small but nevertheless at the same time $\delta^{anh} > \delta^{tun}$. In such a case the energy spectrum of quantum problem near the extremum may be represented as a spectrum of a k -fold 2D-dimensional isotropic (slightly anharmonic) oscillator. It means that each polyad of 2D-isotropic (slightly anharmonic) harmonic oscillator is replaced by a k -fold cluster of similar polyads.

Typically for model problem with anisotropic harmonic oscillator we can neglect the anharmonicity correction and assume equally that $\delta^{tun} < \delta^{ani}$. In such a case the energy spectrum of quantum problem near the minimum or maximum may be represented as a spectrum of a k -fold 2D dimensional anisotropic harmonic oscillator. It means that each nondegenerate level of 2D-anisotropic harmonic oscillator is replaced by a k -fold cluster of energy levels. If both δ^{tun} and δ^{an} are small and have the same order of magnitude, then polyads are

formed by energy levels of each almost isotropic harmonic oscillator and the total energy level pattern is a system of k -fold clusters of vibrational polyads. Internal structure of each cluster depends on the relation between δ^{tun} and δ^{an} and may be complicated and vary significantly from one polyad to another because the ratio between anisotropic and tunneling splitting changes with the vibrational energy increase.

V. MANIFESTATION OF QUALITATIVE EFFECTS IN PHYSICAL SYSTEMS. HYDROGEN ATOM IN MAGNETIC AND ELECTRIC FIELD.

Hydrogen atom in magnetic and electric field gives us opportunity to study the dependence of Rydberg n multiplets on variable parameters such as strength of electric and magnetic fields. To apply directly our approach we should remind once more that external fields are sufficiently low to ensure the small splitting of n multiplets with respect to the splitting between multiplets. In the case of nonzero electric field the ionization is always possible and consequently the strict non-relativistic Hamiltonian of the hydrogen atom in external electric field possesses everywhere continuous spectrum. We will neglect here the effect of ionization and restrict ourselves with the analysis of effective Hamiltonians diagonal in n .

To see the limits of the applicability of the present treatment in the case of a Rydberg atom in an exter-

nal magnetic field, for example, we find here conditions which enable one to treat n -multiplets separately. It is sufficient that the diamagnetic shift which roughly varies as $G^2 n^4$ (G is a magnetic field strength in atomic units, 1 a.u. = $2.35 \cdot 10^5$ T) remains smaller than the energy difference between two consecutive multiplets ($\Delta E = 1/2n^2 - 1/2(n+1)^2 \sim 1/n^3$), i.e. $Gn^{7/2} < 1$. This estimation shows that for sufficiently low magnetic field G we can always find relatively high n shell (to ensure the applicability of the classical approach) which can be analyzed in terms of effective Hamiltonian for an isolated n .

A. Different field configurations and their symmetry.

The qualitative description of the hydrogen atom in two external fields depends strongly on the symmetry of the problem created by two fields. To precise the symmetry we define first the absolute configuration of two fields in the laboratory fixed frame. It is specified by two vectors: $\mathbf{F}$ - the electric field (polar) vector and $\mathbf{G}$ - the magnetic field (axial) vector. Any two absolute configurations which can be transformed one into another by some rotation of the laboratory frame should be considered as physically equivalent and form one (relative) configuration of two fields. This means that the classification of different relative configurations of two fields is equivalent to the classification of orbits of the $O(3)$ group on the six-dimensional space generated by one polar and one axial vector.

Three parameters, F^2 , G^2 , and the scalar product $(\mathbf{F}\mathbf{G})$ with natural relation between them $(\mathbf{F}\mathbf{G})^2 \leq F^2 G^2$, are needed to characterize completely all relative configurations of two fields. Thus the one-to-one correspondence exists between different relative configurations of two fields and points of the filled cone in the 3- D -space (see Fig. 16). The cone shown in Fig. 16 is the orbifold of the $O(3)$ group action on the space of absolute field configurations. Qualitatively different relative configurations are characterized by different symmetry groups. There are six different types of field configurations which are listed in Table XXII together with their symmetry groups.

Let us precise now symmetry groups introduced in Table XXII to characterize different types of field configurations. In each case the complete symmetry group includes two kinds of symmetry operations: purely geometrical spatial transformations forming one of the standard point symmetry groups and symmetry operations related to time reversal.

We use the following notation. The group T includes two elements, identity E and time reversal T . The group T_s includes also two elements, identity E and the symmetry operation $(T\sigma)$ which is the product of the time reversal and the reflection in a plane including both fields. Group G_4 includes four symmetry elements: identity E ,

FIG. 16. Geometrical representations of different field configurations. $\mathbf{F}$ - electric field vector, $\mathbf{G}$ - magnetic field vector.

reflection in the plane orthogonal to the magnetic field σ_h , product $T\sigma$ of time reversal T and reflection σ in plane formed by two orthogonal fields, and the symmetry operation TC_2 which is the product of the time reversal T and the C_2 rotation around the electric field direction. G_4 has three subgroups of order two: $C_s = (E, \sigma_h)$, $T_s = (E, T\sigma)$, and $T_2 = (E, TC_2)$.

We can study now the dependence of the dynamics on the ratio of field strengths assuming that the total effect of both fields is kept to be more or less the same even if we change the field configuration from that corresponding to pure Zeeman effect till that of pure Stark effect. These field configurations lie in some section of the cone in Fig. 16. To make an interesting section of it we take into account that the energy correction to hydrogen atom in the linear Zeeman limit is $\Delta E_n \approx \pm Gn^3$ and in the linear Stark limit is $\Delta E_n \approx \pm 3Fn^4$ where n is the principal quantum number for perturbed hydrogen atom $n \approx \sqrt{-1/(2E)}$. Thus for given n it is natural to fix $S = \sqrt{(Gn^3)^2 + (3Fn^4)^2}$ and to vary only the relative strength of two fields:

$$G_s = \frac{Gn^3}{\sqrt{(Gn^3)^2 + (3Fn^4)^2}}; \quad (138a)$$

$$F_s = \frac{3Fn^4}{\sqrt{(Gn^3)^2 + (3Fn^4)^2}} \quad (138b)$$

We consider the case of small S but we allow large variations of relative strengths of two fields $0 \leq F_s, G_s \leq 1$ with the restriction $F_s^2 + G_s^2 = 1$.

A very interesting question concerns the qualitative behavior of the n -shell dynamics under the variation of field parameters (assuming S to be small enough). Are effective Hamiltonians for n -shell always of the simplest

TABLE XXII. Symmetry classification of relative configurations of the electric field $\mathbf{F}$ and the magnetic field $\mathbf{G}$.

Defining equations	Geometrical description	Symmetry group	Physical problem
$G^2 = F^2 = 0$	point O	$O(3) \wedge T$	no fields
$G^2 = 0, F^2 > 0$	ray OF^2	$C_{\infty v} \wedge T$	Stark effect
$G^2 > 0, F^2 = 0$	ray OG^2	$C_{\infty h} \wedge T_s$	Zeeman effect
$G^2 > 0, F^2 > 0, (\mathbf{GF})^2 = G^2 F^2$	conical surface	$C_{\infty} \wedge T_s$	parallel fields
$G^2 > 0, F^2 > 0, (\mathbf{GF}) = 0$	plane $G^2 OF^2$	G_4	orthogonal fields
$G^2 > 0, F^2 > 0, (\mathbf{GF})^2 < G^2 F^2, (\mathbf{GF}) \neq 0$	interior of the cone	T_s	generic configuration

Morse type? Or there are some region in the space of parameters where the effective Hamiltonian should possess more than minimal number of the stationary points. If such a region exists it means that under the variation of field parameters (even for low field limit) some bifurcations are present and the qualitative modifications of the dynamics take place. Two important cases to study are the case of two parallel fields (configurations of fields represented by points on the surface of cone in Fig. 16) and the case of orthogonal fields (configurations represented by points on the bissectral plane of the cone in Fig. 16). But before looking on these cases we will briefly apply the qualitative analysis to the limiting case of the Zeeman effect.

B. Quadratic Zeeman effect in hydrogen atom

Let consider the Hamiltonian for the quadratic Zeeman effect

$$H = \frac{p^2}{2} - \frac{1}{r} + \frac{G^2}{8}(x^2 + y^2). \quad (139)$$

This Hamiltonian is very popular from the point of view of theoretical investigations of different dynamical regimes in quasiregular and chaotic regions (Braun, 1993; Delande and Gay, 1986; Delos, 1983; Fano, 1992; Farrelly and Krantzman, 1991; Farrelly and Milligan, 1992; Friedrich and Wintgen, 1989; Herrick, 1982; Huppner, 1996; Krantzman, 1992; Kuwata, 1990; Liu, 1996; Mao and Delos, 1992; Robnik and Schrfer, 1985; Sadovskii *et al.*, 1995; Solov'ev, 1981, 1982; Tanner, 1996; Uzer, 1990).

The Hamiltonian (139) is $D_{\infty h} \wedge T$ invariant. Remark that its symmetry is higher than that of an atom under the presence of magnetic field (which is $C_{\infty h} \wedge T_s$) because we neglect the terms linear in angular momentum. Consequently any effective diagonal in n operator can be rewritten in terms of operators corresponding to $D_{\infty h}$ polynomial invariants, ξ, μ^2, ν^2 (see (121, 122b)). The auxiliary invariant $\nu\sigma$ does not enter in the Hamiltonian (139) due to additional time reversal invariance. We replace Hamiltonian (139) by the diagonal in n effective operator just by projecting it on the manifold of the non-perturbed hydrogen atom wave-functions with given n quantum number. Such procedure is physically meaningful in the low magnetic field limit.

The explicit expressions for the diagonal in n matrix elements of the diamagnetic terms are either diagonal in l or nondiagonal in l with $\Delta l = \pm 2$ (they are diagonal in m). It is necessary to find such combinations of diagonal in n operators which give the same matrix elements as the diamagnetic perturbation.

The diagonal in n perturbation of the hydrogen atom may be equivalently represented in the form of the effective operator identical to that used by Solov'ev (1981), Herrick (1992) Delande and Gay (1986) and many others. In terms of invariant polynomials the Hamiltonian for the n shell has the following form

$$H_n = \text{const} + G^2 \frac{n^2(n^2-1)}{16} [\mu^2 - 2\xi - 5\nu^2] \quad (140)$$

where *const* is n -dependent. This Hamiltonian (140) is invariant with respect to the $D_{\infty h} \wedge T$ group. Its action on the phase space of the reduced problem (n -shell effective Hamiltonian) is summarized in Table XVII. Energy levels of this Hamiltonian can be trivially visualized on the $D_{\infty h} \wedge T$ orbifold. The energy function is linear in invariant polynomials used to construct the orbifold. Let analyze now the essential part of the Hamiltonian:

$$\mu^2 - 2\xi - 5\nu^2 \quad (141)$$

There are four critical orbits and the topological structure of the energy levels varies by passing through the critical orbits only. Corresponding energies are (in increased order) $E = -3, C_{\infty v} \wedge T$ - critical orbit; $E = -2, C_{2h} \wedge T$ - critical orbit (one-dimensional manifold); $E = -1, C_{\infty h} \wedge T$ - critical orbit; $E = 2, C_{2v} \wedge T$ - critical orbit (one-dimensional manifold). So, the Rydberg multiplet in relative units lies between $-3 < E < 2$. It is split into three different regions. The lowest one occupies 1/5 of the multiplet width. The highest one occupies 3/5 of the multiplet width (see Fig. 17). Let consider the lowest part of the multiplet. The energy surface near the minimum may be represented as the energy surface for two equivalent 2D slightly anharmonic oscillators. Energy levels form polyads. The n -th polyad consists of $2n$ levels. There are two effects which lead to splitting of the energy levels within a polyad: anharmonicity of the isotropic oscillator and the tunneling between two equivalent wells. The splitting of polyad due to anharmonicity effects preserves the C_{∞} symmetry. As a consequence, the degeneracy of energy levels with the same $|m|$, the projection of the angular momentum, is present.

FIG. 17. Qualitative description of critical orbits versus energy for effective $D_{\infty h}$ -invariant Hamiltonian for quadratic Zeeman effect.

If we neglect the tunneling splitting, for any $|m| \neq 0$ there are four degenerate energy levels. The numerical results for the quantum problem clearly show this patterns. We can estimate the position of the classical energy minimum for the $C_{\infty v}$ orbit from quantum results by assuming the harmonic oscillator model and taking the energy of the zero level equal to the fundamental frequency (this is the linear approximation). Thus for example, for $n = 45$ the harmonic frequency (the fundamental transition) is 0.09442 and the estimated energy of the classical energy minimum found from the entirely quantum calculations is $E_{lin}(C_{\infty v}) = -2.99797$ as compared to (-3) for purely classical model.

At the another end of the energy multiplet (C_{2v}) orbit the energy level pattern is similar to that of one dimensional rotator plus one-dimensional oscillator. One dimensional harmonic oscillator describes energy levels with $m = 0$. The harmonic frequency (for $n = 45$) can be again estimated from the quantum calculations as fundamental transition. It is equal to 0.194414. Adding the half quanta of the corresponding harmonic frequency to the highest (extremal) quantum energy level gives the estimation for the classical energy of the (C_{2v}) critical orbit: $E_{lin}(C_{2v}) = 1.99987$ as compared with $E = 2$ in the classical limit. This numerical comparison is completely satisfactory taking into account the extreme simplicity of the classical model.

It is clearly seen from the numerical results that the $m = 0$ energy levels form the regular sequence of non-degenerate energy levels within the energy interval $2 \geq E \geq -1$ and the regular sequence of doublets within the energy interval $-2 \geq E \geq -3$. This fact well correlate with the energy of the critical orbit C_{2h} characterizing by the energy $E(C_{2h}) = -2$.

It is important to note that the existence of four critical orbits is the consequence of the symmetry of the Hamiltonian and does not depend on the concrete form of the Hamiltonian. At the same time the relative positions in

energy of critical orbit strictly depend on the concrete form of the operator.

C. Hydrogen atom in parallel electric and magnetic fields

We demonstrate shortly in this section one particular application of the qualitative analysis of Rydberg states by studying the transition from a Zeeman to a Stark structure of a weakly split Rydberg n -multiplet of the H atom in parallel magnetic and electric fields (Sadovskii, Zhilinskii, and Michel, 1996). The geometrical approach clearly shows the origin of the new phenomenon, the collapse of the energy levels. The use of classical mechanics, topology, and group theory provides detailed description of the modifications of dynamics due to the variation of the electric field. We focus on the point where the collapse of the Zeeman structure occurs, give the sequence of classical bifurcations responsible for the transition between different dynamic regimes, and compare it to the quantum energy-level structure.

In fact, Rydberg atoms in parallel magnetic and electric fields have been extensively studied both theoretically and experimentally during the last decade. In particular, many studies have focused on the situation where the fields are (relatively) weak and the dynamics can be analyzed in terms of additional approximate integrals of motion (Braun, 1993; Braun and Solov'ev, 1984; Cacciani, 1988, 1989, 1992; Delande and Gay, 1991; Farrelly, Uzer, *et al.*, 1992; Iken, 1994; Seipp, 1996; Veldt, 1993). We use a similar idea to analyze several dynamic regimes that exist for different strength of the electric (F) and magnetic (G) fields. These regimes clearly manifest themselves in the energy level pattern in Fig. 18. At very weak electric field, where most of the studies (see Fig. 19 and discussion in the subsection V B). When F increases this structure quickly disappears. Instead we observe regular "resonance" structures at certain values of F (see Fig. 18). This culminates in an almost complete collapse of the internal structure. Surprisingly, and contrary to the $F \sim 0$ case the dynamics near this collapse has not been earlier analyzed in details.

Neglecting the spin effects the Hamiltonian for the hydrogen atom in constant parallel magnetic G and electric F fields (along the z axis) has the form (in atomic units)

$$H = \frac{p^2}{2} - \frac{1}{r} + \frac{G}{2} L_z + \frac{G^2}{8} (x^2 + y^2) - Fz, \quad (142)$$

with G and F in units of 2.35×10^5 T and 5.14×10^9 V/cm. We restrict ourselves to the low field case where the splitting of an n shell caused by both fields is small compared to the splitting between neighboring n -shells (see Fig. 20). As is well known, in the absence of electric field low- m submanifolds of the n -shell show characteristic pattern of the second order Zeeman effect. When the electric field effect is of the same order as the quadratic

FIG. 18. Collapse of the Zeeman structure for the magnetic field $G = 0.06$ due to the increasing electric field. Quantum levels are calculated for the $n = 10$ multiplet of the hydrogen atom. Scaled electric field strength is given in units $\tilde{F}_0 = \tilde{G}/3$ [see Eq. (144)].

Zeeman effect (see Fig. 19), this pattern disappears and turns into a Stark structure for each m submanifold (Braun and Solov'ev, 1984; Delande and Gay, 1991). Much lesser attention has been paid to the region where the Stark splitting of the n shell ($\propto 3Fn^2$) is of the same order as the n shell splitting due to magnetic field ($\propto Gn$) (Fig. 18), in other words when

$$F_0 = G/(3n). \quad (143)$$

Equation (143) gives the collapse condition for shell n . To insure that this collapse happens when the n -shell splitting remains small compared to the gap between n shells we take $G < 1/n^4$. Under this assumption we can study an isolated n -shell and can use scaling

$$\tilde{F} = Fn^4, \quad \tilde{G} = Gn^3, \quad \tilde{E}_n = 2n^2 E_n + 1, \quad (144)$$

to remove n from the effective n -shell Hamiltonian [Eq. (148) below].

Our purpose is to study the dynamics under the variation of the electric field F in the neighborhood of its critical value. The natural parameter for this study is $\delta = 3Fn/G - 1$.

The analysis is based on the transformation of the initial Hamiltonian (142) into an effective one for an individual n -shell. This can be done either by quantum or by classical perturbation theory (Delande and Gay, 1986; Farrelly, Uzer, *et al.*, 1992; Solov'ev, 1981; Stiefel, 1971).

An effective n -shell Hamiltonian can be expressed in terms of angular momentum $\mathbf{L}$ and Runge-Lenz vector $\mathbf{A} = \mathbf{p} \times \mathbf{L} - \mathbf{r}/r$, or, alternatively, in terms of their linear combinations $\mathbf{J}_1 = (\mathbf{L} + \mathbf{A})/2$ and $\mathbf{J}_2 = (\mathbf{L} - \mathbf{A})/2$.

FIG. 19. Deformation of the QZE structure of the $n = 10$, $m = 0$ multiplet of the hydrogen atom. Dashed lines show the energy in stationary points of classical Hamiltonian restricted on $\mu = 0$.

For the linear Stark-Zeeman effect in parallel fields the effective Hamiltonian is

$$H = \frac{1}{2n^2}(-1 + Gn^2 L_z + 3Fn^3 A_z). \quad (145a)$$

If we impose the relation between field strengths (143) this Hamiltonian becomes

$$H = \frac{1}{2n^2}(-1 + 3F_0 n^3 (J_1)_z). \quad (145b)$$

The n^2 energy levels in the n -shell described by (145b) form n -fold degenerate groups. The levels in each group are labeled by the same value of $(J_1)_z$ and by different values of $(J_2)_z$. Figure 18 shows how the Zeeman structure of the n -shell at $f = 0$ transforms into this highly degenerate structure at $F = F_0$ ($\tilde{F} = \tilde{G}/3$). We call this effect the collapse of the Zeeman structure caused by electric field. To describe the fine structure of each $(J_1)_z$ manifold of states the second order effects should be taken into account.

To develop the effective n -shell Hamiltonian to higher orders we consider n as an integral of motion and use the perturbation theory to reduce the initial problem (142) to two degrees of freedom. Naturally, the pair (L_z, ϕ_{L_z}) describes one of these degrees; the other degree can be described by A_z and ϕ_{A_z} (Farrelly, Uzer, *et al.*, 1992). Of course, for Hamiltonian (142) L_z is strictly conserved and the n -shell Hamiltonian does not depend on ϕ_{L_z} . However, to study the collapse we should consider the energy level structure of the n -shell as a whole, and therefore, we should keep L_z as a dynamical variable. Hence our n -shell Hamiltonian is a function of dynamical variables (L_z, A_z, ϕ_{A_z}) and parameters (n, F, G) .

The classical phase space Σ for effective n -shell Hamiltonian is a 4-D space with topology $S_2 \times S_2$ (S_2 is a 2D

FIG. 20. Neighboring Rydberg multiplets $n = 9, 10, 11$ of the hydrogen atom.

sphere). Its parameterization can be done either using $\mathbf{L}, \mathbf{A}$ variables with $\mathbf{L}^2 + \mathbf{A}^2 = n^2$, and $\mathbf{L} \cdot \mathbf{A} = 0$, or using $\mathbf{J}_1, \mathbf{J}_2$ variables with $\mathbf{J}_1^2 = \mathbf{J}_2^2 = n^2/4$. (In the classical limit n is sufficiently large and $n^2 \approx n^2 - 1$.)

For the qualitative analysis of the n -shell dynamics special variables

$$\nu = A_z/n; \quad \mu = L_z/n; \quad \xi = (L^2 - A^2)/n^2. \quad (146)$$

are the most useful. This choice of variables (146) is based on group theory and, in particular, on invariant theory. In fact, (ν, μ, ξ) form the set of invariant polynomials (the integrity basis) which is used both to label the points of the phase space and to expand the Hamilton function as explained in Section II B. Furthermore, the proper scaling in (146) and (144) results in equations which do not depend on n .

The symmetry group $\mathcal{G}$ of the problem is made of the rotations r_θ and operations (Ts_ϕ) . r_θ are rotations around the “vertical” axis oz , the common direction of the electric and magnetic field; they form the group C_∞ . Each operation (Ts_ϕ) is a product of time reversal T and reflection s_ϕ through a vertical plane that contains oz and has azimuth ϕ . We emphasize that neither T nor s_ϕ are separately a symmetry of the problem. We verify that $(Ts_\phi)^2 = 1$, $(Ts_\phi)r_\theta(Ts_\phi) = r_{-\theta} = r_\theta^{-1}$, $r_\theta(Ts_\phi)(r_\theta)^{-1} = Ts_{\phi+\theta}$. So $\mathcal{G}$ is isomorphic (but not identical) to the group $C_{\infty v}$ and the (Ts_ϕ) ’s form one conjugacy class of $\mathcal{G}$.

Consecutive steps in the qualitative analysis of an effective Hamiltonian under the presence of the symmetry group (Sadovskii and Zhilinskii, 1993a) which are summarized in Section II D includes the study of the action of the symmetry group on the classical phase space, construction of the space of orbits (orbifold), and the analysis of the system of stationary points (orbits) of the

Hamilton function using the topological and group theoretical information about the phase space. To study the action of $\mathcal{G}$ on Σ we just need the following facts: $\mathbf{L}$, and $\mathbf{A}$ are, respectively, axial and polar vectors, and T reverses $\mathbf{L}$. This allows us to find all orbits of the action of the group $\mathcal{G}$ on Σ . According to the general theory of invariants, different orbits can be distinguished by three (algebraically independent) invariants of $\mathcal{G}$ and every smooth $\mathcal{G}$ -invariant function on Σ is a smooth function of these invariants. We have chosen ν, μ, ξ in (146) as these basic invariants. The possible range of variation of ν, μ, ξ is given by a $\mathcal{G}$ -invariant function $\sigma^2 = ((\mathbf{L} \times \mathbf{A}) \cdot \mathbf{n})^2$, with $\mathbf{n}$ the unit vector of oz . It is a polynomial of ν, μ, ξ and it gives a representation of the space of orbits $\mathcal{O}$ (see Fig. 13):

$$\mathcal{O}: \quad -1 \leq \xi \leq 1, \quad 4\sigma^2 = 1 - \xi^2 - 2(1 - \xi)\mu^2 - 2(1 + \xi)\nu^2 \geq 0. \quad (147)$$

Every orbit is represented by a point of $\mathcal{O}$. There are three strata (see Tables X and XV). They contain respectively

- (i) 4 fixed points A, B, C, D , with $\mathcal{G}$ the stabilizer; these 4 points are also called 4 critical orbits since they are extrema of any $\mathcal{G}$ invariant function on Σ (see Section II B 2); their coordinates (ν, μ, ξ) are given in Fig. 13.
- (ii) a two parameter family of circles S_1 (orbits of C_∞) whose points have $\{1, Ts_\phi\}$ as stabilizers; these orbits belong to the boundary of $\mathcal{O}$ given by the equation $\sigma = 0$; remark that this boundary contains the edges of the tetrahedron with vertices A, B, C, D .
- (iii) a three parameter family of generic orbits made of a pair of circles ($= 2S_1$) with trivial stabilizer 1 (internal points of the orbifold).

The Hamilton function can be expressed as a polynomial $H = H(\nu, \mu, \xi)$ of invariant polynomials ν, μ, ξ . Up to quadratic in F and G terms the scaled energy $\tilde{E}$ has the form

$$\tilde{E} = \tilde{G}\mu + 3\tilde{F}\nu - \frac{1}{4}\tilde{G}^2\xi + \frac{1}{8}(9\tilde{F}^2 + \tilde{G}^2)\mu^2 + \frac{1}{8}(3\tilde{F}^2 - 5\tilde{G}^2)\nu^2 + \frac{1}{8}(3\tilde{G}^2 - 17\tilde{F}^2) \quad (148)$$

To qualitatively characterize classical and quantum dynamics we find the system of stationary points (manifolds) of the energy function on the phase space. Group theory asserts that four points A, B, C, D (critical orbits) must be stationary for any smooth function defined over the phase space (see Section II B 2). Energy values (148) at these points are shown in Figs. 18 and 20. Morse inequalities confirm that the simplest Morse-type functions possessing stationary points only on the four critical orbits really exist on Σ and have one minimum, one maximum, and two saddle points. For more complicated functions any other stationary points can be found by looking for those energy sections of orbifold which correspond to the modification of the topology of the energy section.

Simple geometrical analysis shows that in the linear (in F and G) approximation for $F < F_0$ the energy function is of the simplest type with minimum in B , maximum in A , and two saddle points in C and D . For $F > F_0$ the energy function is again of the simplest type with minimum in D , maximum in C , and two saddle points in A and B . Sudden transition from one simplest type of the energy function to another in the linear model occurs due to the formation of the degenerate stationary manifold at value $F = F_0$ corresponding to Hamiltonian (145b). In the linear model the energy surface touches the orbifold through the whole interval $[C, A]$ or $[B, D]$. Introduction of the F^2 and G^2 terms into the energy function removes this degeneracy. The energy surface (148) is the second order surface in ξ, μ, ν variables. It can touch orbifold $\mathcal{O}$ at some isolated points on the $\sigma = 0$ surface which are different from the critical orbits A, B, C, D . If this happens, additional stationary orbits are present. The detailed analysis of a system of stationary points as a function of F near the collapse value F_0 shows how the transformation from the Zeeman type energy function (with only four stationary critical orbits having minimum and maximum in B and A) to the Stark type energy function (with only four stationary critical orbits having minimum and maximum in D and C) occurs. Two sequences of bifurcations are present with two bifurcations in each sequence. As F increases, one sequence begins with a bifurcation at point B which creates a new stationary S_1 orbit of $\tilde{E}$ on Σ . The corresponding point on the surface of the orbifold moves from B to D and disappears at D after the second bifurcation. Another sequence of bifurcations proceeds in the similar way with two bifurcations at C and A and the new additional stationary orbit moving from C to A .

Positions of all stationary orbits can be found by solving the Hamiltonian equations on Σ . Alternative way is to use the geometrical representation of the orbifold and of the energy surface. To find noncritical stationary orbits we find points where the energy surface touches the orbifold. In other words we find points where the normal vector to the $\sigma = 0$ surface and the normal vector to the energy surface $\mathbf{k} = (k_\nu, k_\mu, k_\xi)$ are collinear. This geometric view gives us extremely simple conditions for bifurcations at points A, B, C, D .

$$A: 4k_\xi k_\mu = k_\nu^2 - k_\mu^2; \quad \delta_A \approx -\tilde{G}^2/8 - \tilde{G}^3/16, \quad (149a)$$

$$C: 4k_\xi k_\nu = k_\nu^2 - k_\mu^2; \quad \delta_C \approx 2\tilde{G}/3 + \tilde{G}^2/72, \quad (149b)$$

$$B: 4k_\xi k_\mu = k_\mu^2 - k_\nu^2; \quad \delta_B \approx -\tilde{G}^2/8 + \tilde{G}^3/16, \quad (149c)$$

$$D: 4k_\xi k_\nu = k_\mu^2 - k_\nu^2; \quad \delta_D \approx -2\tilde{G}/3 + \tilde{G}^2/72. \quad (149d)$$

When δ varies between δ_A and δ_C an additional stationary orbit exists on the surface of the orbifold and moves from the point A to the point C . Similarly for δ between δ_D and δ_B another additional stationary orbit moves from D to B . The energies of all stationary orbits near the bifurcation points and the quantum energy levels are shown in Fig. 21.

FIG. 21. Bifurcation diagram near the collapse region. Classical (left) versus quantum (right) representation.

Simple quantum mechanical interpretation of the effect of the transformation of the Zeeman-type structure into the Stark-type one can be done by looking at the two extremal states (with minimal and maximal energy) of the same n multiplet (Fig. 21). We can characterize each extremal state by two average values $\langle L_z \rangle$ and $\langle A_z \rangle$. From the positions of stationary points on the orbifold it follows immediately that for the state with maximal energy $\langle L_z \rangle \approx n$ for $\delta < \delta_A$, $\langle L_z \rangle \approx 0$ for $\delta > \delta_C$, whereas $\langle L_z \rangle$ varies almost linearly with δ for $\delta_A < \delta < \delta_C$. For the same state $\langle A_z \rangle \approx 0$ for $\delta < \delta_A$, $\langle A_z \rangle \approx n$ for $\delta > \delta_C$, whereas $\langle A_z \rangle$ varies almost linearly with δ for $\delta_A < \delta < \delta_C$.

We conclude that important qualitative modifications of dynamics take place in the collapse region. This suggests new experimental investigations which can use the detailed information on many energy-level crossings in the collapse region to obtain quantum states with desired properties by fine tuning of the field parameters. Existence of collapsed levels with different projections of the orbital momentum m can be used in the experiment to selectively produce states with any possible m using adiabatic change of field parameters. This is specially important for formation of so-called “circular” states with very high $m \sim n$ values (Delande and Gay, 1988; Germann, 1995; Hulet and Kleppner, 1983; Kalinsky, 1996a, 1996b).

D. Hydrogen atom in orthogonal electric and magnetic fields

Hydrogen atom in crossed (orthogonal) electric and magnetic fields was the subject of many experimental (Flöthmann, 1994; Raithel, Fauth, and Walter, 1991,

1993; Raithel and Fauth, 1995; Rinneberg, 1985) and theoretical (Farrelly, 1994; Gourlay, 1993; Milczewski, 1994, 1996) studies. The purpose of this Section is to show what kind of qualitative information can be obtained taking into account only general topology and symmetry information.

The hydrogen atom in the presence of two orthogonal fields gives us an example of system with the finite symmetry group G_4 (see sections IIII and V A). The space of orbits in this case is four dimensional and it is naturally more difficult to visualize its stratification and to represent the orbifold in a geometrical way. Nevertheless very useful topological and group-theoretical information can be found by study the invariant subspaces of different symmetry. We remind on this example again major steps of the qualitative analysis mentioned in Sections II and III and leave the details for further publications.

First we construct the Molien function and the integrity basis for the ring of G_4 invariant polynomials on Σ . The procedure we follow here is formally the same as that used in Appendix B for molecular point symmetry groups.

The simplest way to write the Molien function is to work in $\mathbf{J}_1, \mathbf{J}_2$ representation, to consider the ring of all invariant functions constructed from six dynamic variables and to restrict this ring to 4D classical phase space, Σ . We start with the situation without any additional symmetry (the symmetry group is trivial, C_1). On the six dimensional space $(J_1)_\alpha, (J_2)_\beta$, $(\alpha, \beta = x, y, z)$ the Molien function for invariants has a trivial form

$$M_{C_1} = \frac{1}{(1-\lambda)^6}. \quad (150)$$

The ring of the invariant polynomials on the 6D-space $\mathcal{P}_6^{C_1}$ is the ring of all polynomials

$$\mathcal{P}_6^{C_1} = P[(J_1)_x, (J_1)_y, (J_1)_z, (J_2)_x, (J_2)_y, (J_2)_z]. \quad (151)$$

To restrict the polynomial ring on the submanifold

$$\theta_5 = (J_1)_x^2 + (J_1)_y^2 + (J_1)_z^2 = \text{Const}, \quad (152a)$$

$$\theta_6 = (J_2)_x^2 + (J_2)_y^2 + (J_2)_z^2 = \text{Const}, \quad (152b)$$

we are obliged to introduce two second order polynomials, θ_5, θ_6 given by (152) as denominator invariants. This may be done by multiplying both the numerator and denominator of the Molien function (150) by $(1+\lambda)^2$. The new form of the Molien function

$$M_{C_1} = \frac{1+2\lambda+\lambda^2}{(1-\lambda)^4(1-\lambda^2)^2} \quad (153)$$

corresponds now to another description of the ring of invariants $\mathcal{P}_6^{C_1}$ which is considered as a free module

$$\begin{aligned} \mathcal{P}_6^{C_1} = & P[(J_1)_x, (J_1)_y, \theta_5, (J_2)_x, (J_2)_y, \theta_6] \\ & \bullet (1, (J_1)_z)(1, (J_2)_z) \end{aligned} \quad (154)$$

with four auxiliary invariants $\varphi_1 = 1$, $\varphi_2 = (J_1)_z$, $\varphi_3 = (J_2)_z$, $\varphi_4 = (J_1)_z(J_2)_z$. We use the notation $(a, b)(c, d) =$

(ac, ad, bc, bd) to show that four numerator invariants are represented as product of more simple terms. Having the form (153) of the Molien function and the form (154) of the module of invariant functions it is easy to make the restriction to the submanifold Σ . We just eliminate two denominator invariants, θ_5, θ_6 , corresponding to the equations defining Σ . The resulting Molien function and the module of invariants on Σ are written as follows:

$$M_{C_1}|_\Sigma = \frac{1+2\lambda+\lambda^2}{(1-\lambda)^4}, \quad (155a)$$

$$\begin{aligned} \mathcal{P}^{C_1}|_\Sigma = & P[(J_1)_x, (J_1)_y, (J_2)_x, (J_2)_y] \\ & \bullet (1, (J_1)_z)(1, (J_2)_z). \end{aligned} \quad (155b)$$

The choice of basic and auxiliary invariants is ambiguous and that proposed here is just an example. The important point is that the integrity basis may be constructed which includes four numerator invariants (including 1) and four denominator invariants.

To find now the IB in $\mathbf{A}, \mathbf{L}$ representation we can simply transform invariants from $\mathbf{J}_1, \mathbf{J}_2$ to $\mathbf{A}, \mathbf{L}$ representation.

Let now increase slightly the symmetry and consider the case of symmetry corresponding to two non-parallel non-orthogonal fields. The finite symmetry group in this case has order 2 and includes one nontrivial operation: product of time reversal and space reflection in the plane defined by two fields. To precise the action of the symmetry group on basis polynomials we fix the coordinate frame in such a way that say x -axis coincides with the electric field vector and the y -axis belongs to the plane of two fields and has the positive projection of the magnetic field on it.

Let $T\sigma$ be the symmetry operation for generic configuration of two fields considered. It follows immediately that A_x, A_y, L_x, L_y are invariant with respect to this symmetry operation, whereas A_z, L_z are pseudo-invariant (change the sign). We see as well, that all basic invariants of the ring of polynomials (154), and (155b) are invariant with respect to the $T\sigma$ operation. At the same time between three nontrivial numerator (auxiliary) invariants only one is invariant with respect to $T\sigma$ operation, whereas two others change sign under this operation. This means that the Molien function and the module of invariants on Σ in the case of generic configuration of two fields has the form

$$M^{2Fgen}|_\Sigma = \frac{1+\lambda^2}{(1-\lambda)^4}, \quad (156a)$$

$$\begin{aligned} \mathcal{P}^{2Fgen}|_\Sigma = & P[(J_1)_x, (J_1)_y, (J_2)_x, (J_2)_y] \\ & \bullet (1, (J_1)_z(J_2)_z). \end{aligned} \quad (156b)$$

The symmetry group for the case of two orthogonal fields is higher. It includes four symmetry elements E - identity, $T\sigma$, introduced just above, σ_{orthB} - reflection in the plane orthogonal to the magnetic field B (this plane includes the electric field vector), and TC_2 - the product of the time reversal and the C_2 rotation around the electric field. For the particular case of orthogonal fields it is

TABLE XXIII. Transformation properties of dynamic variables for two orthogonal fields under the action of G_4 group.

	E	$T\sigma^{(eb)}$	$\sigma^{(ep)}$	$TC_2^{(e)}$
A_e	+	+	+	+
A_b	+	+	-	-
A_p	+	-	+	-
L_e	+	+	-	-
L_b	+	+	+	+
L_p	+	-	-	+
$(J_1)_e$	+	+	$-(J_2)_e$	$-(J_2)_e$
$(J_1)_b$	+	+	$(J_2)_b$	$(J_2)_b$
$(J_2)_e$	+	+	$-(J_1)_e$	$-(J_1)_e$
$(J_2)_b$	+	+	$(J_1)_b$	$(J_1)_b$
$(J_1)_p$	+	-	$-(J_2)_p$	$(J_2)_p$
$(J_2)_p$	+	-	$-(J_1)_p$	$(J_1)_p$
$(J_1)_p(J_2)_p$	+	+	+	+
$(J_1)^2$	+	+	$(J_2)^2$	$(J_2)^2$
$(J_2)^2$	+	+	$(J_1)^2$	$(J_1)^2$

useful to change the notation of axes in order to show explicitly their orientation with respect to external fields. We use below in this section coordinate frame $\{e, b, p\}$ with vector e along the electric field vector, vector b along the magnetic field vector, and vector p chosen to form the right-hand frame.

Symmetry properties of A_α, L_β and of all basic and auxiliary invariants of the module (154) and (156b) are summarized in the Table XXIII.

The first consequence is the necessity to change the two basic invariant which define the submanifold Σ . Instead of $J_1^2 = J_2^2 = \text{const}$ we can use $J_1^2 + J_2^2 = \text{const}$ and $J_1^2 - J_2^2 = 0$. The first transformed equation is invariant with respect to the symmetry group. The second is pseudo-invariant. To deal with invariants only on the 6D-space we should first change the integrity basis by introducing as basic invariants θ_{5a}, θ_{6a} , and as auxiliary invariant φ_{6b} and instead of $(J_1)_e, (J_1)_b, (J_2)_e, (J_2)_b$ their linear combinations which have well defined symmetry properties (irreducible tensors) with respect to the symmetry group

$$\theta_{5a} = (J_1^2 + J_2^2), \quad (157a)$$

$$\theta_{6a} = (J_1^2 - J_2^2)^2, \quad (157b)$$

$$\varphi_{6b} = (J_1^2 - J_2^2), \quad (157c)$$

$$\theta_1 = (J_1)_e - (J_2)_e, \quad (157d)$$

$$\theta_2 = (J_1)_b + (J_2)_b, \quad (157e)$$

$$\theta_3 = (J_1)_e + (J_2)_e, \quad (157f)$$

$$\theta_4 = (J_1)_b - (J_2)_b, \quad (157g)$$

$$\varphi_1 = (J_1)_p - (J_2)_p, \quad (157h)$$

$$\varphi_2 = (J_1)_p + (J_2)_p, \quad (157i)$$

$$\varphi_3 = (J_1)_p(J_2)_p. \quad (157j)$$

Now we have the description of the ring of C_1 invariant polynomial on the 6D-space in terms of the integrity basis which includes invariants and pseudo-invariants of the

symmetry group for two orthogonal fields. The Molien function and the ring of invariants $\mathcal{P}_6^{C_1}$ can be written as

$$M_6^{C_1} = \frac{(1+2\lambda+\lambda^2)(1+\lambda^2)}{(1-\lambda)^4(1-\lambda^2)(1-\lambda^4)}, \quad (158a)$$

$$\mathcal{P}^{C_1}|_6 = P[\theta_1, \theta_2, \theta_3, \theta_4, \theta_{5a}, \theta_{6a}] \quad (158b)$$

$$\bullet (1, \varphi_1, \varphi_2, \varphi_3)(1, \varphi_{6b}).$$

Reduction on Σ should be done now by eliminating two basic invariants, θ_{5a}, θ_{6a} and one auxiliary invariant φ_{6b} which corresponds to zero on Σ . Between basic denominator invariants we have two, (θ_3, θ_4) , which are pseudo-invariants with respect to the total symmetry group of the problem. To insure that all basic numerator polynomials are invariants of the total symmetry group we can change the integrity basis by introducing instead of θ_3, θ_4 two new basic invariants $\theta_{3a} = \theta_3^2, \theta_{4a} = \theta_4^2$ and three auxiliary polynomials $\varphi_{4a} = \theta_3, \varphi_{4b} = \theta_4, \varphi_{4c} = \theta_3\theta_4$.

After such a modification we can rewrite the Molien function on Σ and the module of polynomials on Σ in terms of integrity basis including as basic polynomials only invariant polynomials with respect to the total symmetry group, and as auxiliary polynomials both invariants and pseudo-invariants of the total symmetry group.

$$M_{C_1}|\Sigma = \frac{(1+2\lambda+\lambda^2)(1+\lambda)^2}{(1-\lambda)^2(1-\lambda^2)^2}, \quad (159a)$$

$$\mathcal{P}^{C_1}|\Sigma = P[\theta_1, \theta_2, \theta_{3a}, \theta_{4a}] \quad (159b)$$

$$\bullet (1, \varphi_1, \varphi_2, \varphi_3)(1, \varphi_{4a}, \varphi_{4b}, \varphi_{4c}).$$

The list of polynomials forming the integrity basis is as follows:

$$\theta_1 = A_e; \quad \theta_2 = L_b y; \quad (160a)$$

$$\theta_{3a} = L_e^2; \quad \theta_{4a} = A_b^2; \quad (160b)$$

$$\varphi_1 = A_p; \quad \varphi_2 = L_p; \quad (160c)$$

$$\varphi_3 = (J_1)_p(J_2)_p; \quad (160d)$$

$$\varphi_{4a} = L_e; \quad \varphi_{4b} = A_b; \quad \varphi_{4c} = L_e A_b; \quad (160e)$$

$$\varphi_1 \varphi_{4a}, \quad \varphi_1 \varphi_{4b}, \quad \varphi_1 \varphi_{4c}, \quad (160f)$$

$$\varphi_2 \varphi_{4a}, \quad \varphi_2 \varphi_{4b}, \quad \varphi_2 \varphi_{4c}, \quad (160g)$$

$$\varphi_3 \varphi_{4a}, \quad \varphi_3 \varphi_{4b}, \quad \varphi_3 \varphi_{4c}. \quad (160h)$$

Now we can simply eliminate all auxiliary polynomials which are not invariant with respect to the total symmetry group for two orthogonal fields. This gives the following Molien function and the module of invariant on Σ .

$$M^{2orthF}|\Sigma = \frac{(1+2\lambda^2+\lambda^4)}{(1-\lambda)^2(1-\lambda^2)^2}, \quad (161a)$$

$$\mathcal{P}^{2orthF}|\Sigma = P[A_e, L_b, L_e^2, A_b^2] \quad (161b)$$

$$\bullet (1, L_e A_b, (J_1)_p(J_2)_p, (J_1)_p(J_2)_p L_e A_b). \quad (161c)$$

Remark that we can replace $(J_1)_p(J_2)_p$ by $(L_p^2 - A_p^2)$.

TABLE XXIV. Invariant manifolds for G_4 symmetry group action on Σ . (Hydrogen atom in perpendicular electric and magnetic fields.)

Stabilizer	Dim	Topology	Equations
G_4	1	S_1	$L_b^2 + A_c^2 = 1$
C_s	2	S_2	$L_e^2 = A_b^2 = 0, L_p^2 - A_p^2 \leq 0$
T_2	2	S_2	$L_e^2 = A_b^2 = 0, L_p^2 - A_p^2 \geq 0$
T_s	2	$S_1 \times S_1$	$L_e^2 + L_b^2 + A_c^2 + A_b^2 = 1$
C_1	4	$S^2 \times S^2$	$\Sigma \quad (L^2 + A^2 = 1; (L \cdot A) = 0)$

Next step of the qualitative analysis is the stratification of the phase space Σ under the action of the G_4 symmetry group. Invariant manifolds are listed in Table XXIV. Taking in mind this information we apply the Morse theory arguments to get restrictions on number and location of stationary points of the Hamilton function. As soon as there are no zero dimensional strata of the group action, there is no critical orbits. Nevertheless, we can say that there should be at least two stationary orbits on the G_4 invariant subspace and at least one additional stationary T_s invariant orbit formed by two equivalent points. Under the variation of the strength of two fields these stationary points move but they are obliged to be always on these invariant subspaces.

If we compare results of qualitative analysis of the hydrogen atom in parallel fields with that for hydrogen atom in orthogonal fields it becomes clear that for sufficiently low fields evolution of Zeeman multiplet into Stark multiplet goes through a sequence of bifurcations for parallel fields, whereas for orthogonal fields no generic bifurcations are present. Immediately natural question arises. What can be said about generic field configurations. Is it reasonable to expect the presence of bifurcations under some variation of relative fields and their orientation?

E. Where to look for bifurcations?

To answer this question we represent in Fig. 22 the space of relative configurations of two fields $\mathbf{F}, \mathbf{G}$ imposing the restriction of the type $F^2 + aG^2 = S^2$, where S is supposed to be sufficiently small and the positive parameter a can be chosen to in such a way that the splitting of Rydberg multiplet in Zeeman and Stark limit be approximately the same.

If electric and magnetic fields are noncollinear and nonorthogonal the only nontrivial symmetry operation is the composition of time reversal and the space reflection in the plane including two fields. So the symmetry group for such generic orientation is the T_s group introduced earlier. The only nontrivial invariant subspace is the T_s invariant torus. On this torus four stationary points are generically present. The same four stationary points should always be present for the Σ phase space. The appearance of additional stationary points should be verified first of all near the collinear configuration of

FIG. 22. Schematic representation of qualitatively different Morse type Hamiltonians for hydrogen atom in two external fields (electric and magnetic). Two parameter family of Hamiltonians is split into regions corresponding to the simplest and non-simplest Hamiltonians (as a Morse-type functions).

two fields corresponding to the non-simplest Morse type Hamiltonian. Near this point the Hamiltonian is not of the simplest Morse type as we show below.

Let consider the collinear configuration of two fields corresponding to the range of F, G parameters such that additional extrema on Σ exist. These additional extrema correspond to points on $\sigma = 0$. After a small deformation of the configuration of fields (fields become nonorthogonal after an arbitrarily small perturbation) the symmetry is broken but each stationary orbit leads to one stationary orbit of the lower symmetry group. As soon as for parallel fields on T_s invariant torus (with one particular orientation of symmetry plane) there are more than four stationary points their number should be conserved after the symmetry is broken by small perturbation.

So near the collapse region for parallel fields there should be the region where the Hamiltonian is a non-simplest Morse type function even for non-parallel fields.

Figure 22 demonstrates schematically this fact.

VI. CONCLUSIONS AND PERSPECTIVES

The main idea of this article was to demonstrate how general group-theoretical and topological methods work in a particular physical problem, Rydberg states of atoms and molecules. As compared to similar analysis realized earlier for molecular rotation and vibration, the mathematical difficulty which was overcome in this study is the presence of continuous symmetry related with the generalization from standard Morse theory of functions with isolated non-degenerated stationary points to Morse Bott theory of functions with non-degenerate stationary manifolds. At the same time the general scheme of the qualitative analysis follows the way developed earlier for molecular rotation and vibrations (Pavlichenkov and Zhilinskii,

1988; Sadovskii and Zhilinskii, 1993a; Zhilinskii, 1996).

In contrast to many specific theoretical molecular analysis, we do not impose at the beginning the concrete form of the Hamiltonian. This allows us to find some features of the energy spectrum (or of the classical dynamical behavior) which are common for a relatively large set of possible Hamiltonian functions. The Hamiltonian which is interesting from the point of view of physical applications is sometimes just a single particular operator from the wide set of objects considered. General statements can be surely applied to one particular example but the information getting in such way is certainly more restrictive than the result of concrete numerical analysis of the particular problem. This is a disadvantage of the generic qualitative analysis. Otherwise, conceptually it is extremely useful to understand the presence of features which are independent on the precise form of the Hamiltonian, especially taking into account the fact that any Hamiltonian used for concrete physical application is always an approximation.

For Rydberg problems we have studied very simple and rather restrictive case of small splitting of n -shell. It is certainly possible to find some physical situations when such a model is rather accurate and reasonable. At the same time it is clear that for real molecular and atomic systems there are many interactions (and additional degrees of freedom) which become important and often can modify considerably even the qualitative behavior. Among the simplest but essential corrections are those due to the spin, to the motion of the center of mass under the presence of external fields (Johnson and Hirschfelder, 1983; Farrelly, 1994).

Highly excited states of the hydrogen atom occupied rather special place among Rydberg states of atomic systems with one excited electron. The origin of this is the additional dynamical $O(4)$ symmetry. Many different experimental and theoretical analysis of the nonhydrogenic atom Rydberg states were done. The quantum defect theory is the most popular and powerful tool of the theoretical analysis and interpretation of experimental data. Aymar, Greene, and Luc-Koenig (1996) reviewed recently this subject. At the same time the systematic qualitative analysis of effective n -shell Rydberg Hamiltonians for free nonhydrogenic atoms or atoms in external fields have not still be done.

Doubly-excited Rydberg states of atoms give much more complicated examples with rich qualitative structure remarked initially by Herrick and Sinanoglu (1975) on the basis of comparison of approximate $O(4)$ dynamical symmetry and extensive numerical calculations. To understand better the qualitative features of electronic excited states and especially their localization properties [see for example papers by Goodson and Watson (1993), Dunn *et al.* (1994) and references therein] it would be interesting to perform the topological and symmetry analysis of two-electron problem on the same basis as it is done in the present paper for one-electron Rydberg problem.

We have not practically touched in the present review

the concrete applications of the qualitative theory to Rydberg states of diatomic or polyatomic molecules except for general symmetry analysis. It should be noted that the application of qualitative analysis should be started with the reanalysis of the excited states of the simplest one-electron diatomic molecule H_2^+ . In spite of its apparent simplicity the description of the fine structure of highly excited states of H_2^+ still remains the question of interest (Byers Brown, 1966; Coulson, 1967; Grozdanov and Solov'ev, 1995). Diatomic molecules are of particular theoretical interest due to the presence of continuous symmetry groups which are different for homonuclear and heteronuclear molecules. Due to variety of diatomic molecules it is possible to find examples of molecules with slight or strong breaking of the interchange symmetry of two nuclei. Moreover for a number of diatomic molecules experimental or numerical data exists (Bordas, 1985; Dabrowski, 1992, 1994; Davies, 1990; Fujii, 1994; Harris, 1993; Howard, 1995; Jacobson, 1996; Jungen, 1989, 1990; Kim, 1995; Merkt, 1996; Michels, 1963; Watson, 1994) and experimental data or results of alternative numerical modelization are ready to be compared through the qualitative analysis in order to reveal some universal features of the system of Rydberg states of diatomics.

Between polyatomics the H_3 molecule is surely the most popular as an object to study Rydberg states (Bordas, 1991, 1992; Dodhy, 1988; Helm, 1986, 1988; Herzberg, 1981; Ketterle, 1989; King, 1979; Lembo, 1989, 1990; Pan, 1988; Stephens, 1995). In fact this molecule belong to the class of so-called Rydberg molecules for which the chemical bonding is formed due to Rydberg electron (Herzberg, 1987). One can imagine Rydberg molecule as stable molecular ion plus electron on high Rydberg orbit. Typically Rydberg molecules are bound only in excited electronic states and their predissociation becomes more pronounced under electronic desexcitation. H_3 and NH_4 are typical Rydberg molecules (Herzberg, 1981). More exotic examples of Rydberg dimers like $(H_3)_2$ or $(NH_4)_2$ etc are discussed by Boldyrev (1992a, 1992b) and Wright (1994). Chemical processes related with Rydberg electrons were studied even for such big objects as fullerenes (Weber, 1996) or metal surfaces (Ganesan, 1996).

Comparison of simple model electronic Rydberg calculations with concrete molecular experiments is naturally much more complicated due to presence of additional degrees of freedom (vibration and rotation). At the same time this gives possibility to new qualitative effects like, for example, the stabilization of unstable rotational axis of asymmetrical top molecule due to interaction with Rydberg electron as proposed by Basov and Pavlichenkov (1996) or core induced stabilization of molecular Rydberg states discussed by Lee *et al.* (1994). Monitoring of intramolecular dynamics through preparation of special Rydberg electron wave packets is not now a science fiction but the subject of current interest (Beims and Alber, 1993; Boris, 1993; Dietrich, 1996; Frey, 1996; Jones, 1996;

Rabani, 1996; Remacle, 1996a, 1996b; Thoss, 1995).

Naturally, it is impossible to expect that simple qualitative model based on n -shell approximation can be used in the region where n is no longer an approximate integral of motion. So further natural question arises: How to extend the approach presented in this paper to the case of "overlapping" and to the case of more serious "interactions" of different n -shells. This problem can be attacked from two opposite sides. One possibility is to start with the model of "complete classical chaos" and to study peculiarities of quantum system through some kind of statistical or some other "chaological" methods (Bixon and Jortner, 1996; Friedrich and Wintgen, 1989; Hasegawa, 1989; Lombardi, 1988, 1993; Milczewski, 1996; Zakrzewski, 1995). Alternative approach consists in studying qualitative effects related to violation of individual n -shell approximation. Such extension of the qualitative approach to the qualitative theory allowing the "coupling" of different n -shells should be extremely useful for Rydberg problem for the intermediate region between quasiregular and completely chaotic motion. The analog of such an extension was proposed earlier in the qualitative analysis of molecular rovibrational structure. Rotational multiplets of different individual vibrational components can be considered as formal analogs of different n -multiplets. In the classical limit the violation of individual components (vibrational components for rovibrational problems or n -shells for Rydberg problems) is associated with the formation of "diaboloic" points (conical intersection points) between different energy surfaces.

As was shown on simple initial example by Pavlov-Verevkin, Sadovskii, and Zhilinskii (1988) the new qualitative phenomenon, namely the redistribution of energy levels between different branches in the energy spectrum typically appears in such a case under variation of the integral of the motion. Each elementary qualitative phenomenon can be characterized by a topological invariant which is stable under small deformation of the Hamiltonian. Recent theoretical analysis (Brodersen and Zhilinskii, 1995a, 1995b; Zhilinskii and Brodersen, 1994; Zhilinskii, 1996) supports this point of view and put some interesting relations with rather different physical phenomena like recoupling of angular momenta and quantum Hall effect (Avron, 1983, 1988; Bellissard, 1989; Leboeuf, 1992; Niu, 1985; Simon, 1983) or purely mathematical questions like topological obstructions to integrability (Cushman, 1997; Duistermaat, 1980; Nekhoroshev, 1972).

New qualitative changes similar to the redistribution of energy levels between vibrational components in rovibrational problem are expected to appear generically in Rydberg problem under energy excitation. They are associated with the diaboloic point formation in the classical limit and with the overlapping and regrouping of energy levels in different n -shells. These points are surely new hot points of further theoretical and experimental study.

ACKNOWLEDGEMENTS

Authors acknowledge many fruitful discussions during the work on the present manuscript with Drs. D. Sadovskii, R. Littlejohn, J. Bellissard, D. Delande. M. Gromov helped us to understand better the mathematical problems related with Morse-Bott theory. B.Z. thanks IHES, Bures-sur-Ivette, Université Lille 1, Université de Bourgogne, Aarhus Universitet for financial support. The Laboratoire de Physico-Chimie d'Atmosphère participates in the Centre d'Etude et de Recherches Lasers et Applications, supported by the Ministère chargé de la Recherche, the Région Nord/Pas de Calais and the Fonds Européen de Développement Economique des Régions.

APPENDIX A: GEOMETRICAL REPRESENTATION

We consider in this appendix the geometrical representation of orbifolds which is the initial step for the geometrical representation of qualitatively different types of the Morse Bott type functions defined over classical phase space for various invariance groups. As soon as we are working with functions which are supposed to be the classical analog for quantum effective Hamiltonians, we will use the notion "energy level" for solution of the equation $H = \text{const}$. In our particular case the Hamiltonian function is defined over four dimensional space ($\Sigma = S_2 \times S_2$), so the energy level is normally three dimensional region of the phase space which may be characterized by its topology. Taking into account the action of the symmetry group we can reach more detailed information about the structure of each energy level by indicating the topological structure or orbits from one side and the topological structure of the orbifold section from another side.

1. $O(3)$ or $SO(3)$ invariant Hamiltonian

The case of $SO(3)$ invariant operator is not very interesting in our particular problem because any $SO(3)$ invariant operator is also invariant with respect to the $O(3)$ group on the $\Sigma = S_2 \times S_2$ manifold. So if one is restricted to the consideration of the diagonal in " n " effective operators, there is no difference between $SO(3)$ and $O(3)$ symmetry groups.

The orbifold for the $O(3)$ action on the $\Sigma = S_2 \times S_2$ manifold is shown in Fig.23. From the topological point of view it is a 1D-ball ($\Sigma/O(3) \sim B_1$). Orbits are parameterized by the value of one invariant polynomial, ξ . The detailed description of orbits and strata is given in Table V of this paper. The simplest Morse Bott type function defined on Σ and $O(3)$ invariant possesses two critical manifolds coinciding with two critical orbits of the $O(3)$ group action. Different energy levels of such simplest function are characterized by the topological structure in Table XXV. There are in fact two possible choices

TABLE XXV. Topological description of energy levels for the simplest Morse Bott type Hamiltonian ($O(3)$ invariant). "no" in the Morse index column means absence of stationary points.

Morse index	Dim of orbit	Topological structure of the energy level	Local symmetry
0 (2)	2	$e \times S_2$	$C_{\infty v}$
no	3	$e \times RP^3$	C_s
2 (0)	2	$e \times S_2$	$C_{\infty h}$

FIG. 23. Orbifold for the $O(3)$ group action on $\Sigma = S^2 \times S^2$. Orbits are parameterized by the value of one invariant polynomial, ξ .

of the simplest Morse Bott function differing in interchanging the position of minimum and maximum critical manifolds. As soon as the dimension of critical orbits is two the Morse indexes for minimal or maximal critical manifolds are equal 0 or 2 correspondingly.

Any function $H = H(\xi)$ which has $\frac{\partial H}{\partial \xi} \neq 0$ for $-1 \leq \xi \leq 1$ may be used as an example of the simplest Morse Bott type function.

If we have effective Hamiltonian which possesses an extremum within the interval $-1 < \xi < +1$, then the system of different energy levels has more complicated topological properties. For example, the effective Hamiltonian of the form

$$H = c(\xi + 1/2)^2 \quad (A1)$$

has five topologically different energy levels given in the Table XXVI. The Morse index for the RP^3 stationary manifold may be either 0 or 1 (because the dimension of the RP^3 stationary manifold is 3).

TABLE XXVI. Topological description of energy levels for the (A1) type Hamiltonian ($O(3)$ invariant). Morse indices are indicated for the $c > 0$ ($c < 0$) choice of the parameter. The disconnected components of the energy level are represented within the curly brackets.

Morse index	Topological structure of the energy level	Local symmetry
0(1)	$e \times RP^3$	C_s
no	$2 \{e \times RP^3\}$	C_s
2(0)	$\{e \times S_2\} +$	$C_{\infty v}$
no	$\{e \times RP^3\}$	C_s
no	$e \times RP^3$	C_s
2(0)	$e \times S_2$	$C_{\infty h}$

FIG. 24. Orbifold for the C_∞ group action on $\Sigma = S^2 \times S^2$. Each part of the orbifold is parameterized by the value of three invariant polynomials, ξ, μ, ν .

One can easily see that the total number of critical manifolds may be arbitrary but the numbers of critical manifolds with given indices are related among themselves.

If the total number of critical manifolds is even there are one maximum and one minimum which are situated on critical orbits ($C_{\infty v}$ and $C_{\infty h}$) and equal number of minima and maxima on generic (C_s) orbits. If the total number of critical manifolds is odd there are two maxima (or two minima) on critical orbits ($C_{\infty v}$ and $C_{\infty h}$) and odd, $2p + 1$, (even, $2p$) number of minima and even, $2p$, (odd, $2p + 1$) number of maxima on generic (C_s) orbits ($p \geq 0$ being nonnegative integer).

2. C_∞ invariant Hamiltonian

Orbits for the C_∞ action on Σ are parameterized by values of three denominator invariants (ξ, μ, ν) and one numerator invariant, σ . So, we can represent the orbifold in ξ, μ, ν variables taking into account that for $\sigma^2 = 0$ there is one to one correspondence between points of orbifold and ξ, μ, ν values satisfying in equalities (49). If $\sigma^2 > 0$ there are two orbits with the same ξ, μ, ν values but with the different signs of σ

$$\sigma = \pm \left[\frac{1}{4}(1 - \xi^2) - \frac{1}{2}(1 - \xi)\mu^2 - \frac{1}{2}(1 + \xi)\nu^2 \right]^{1/2}. \quad (A2)$$

We represent orbifold as consisting of two parts, one corresponding to $\sigma \geq 0$ and other corresponding to $\sigma \leq 0$. Both these parts are shown in Fig.24. They are identical in 3D- (ξ, μ, ν) -space. For $\xi = 1$ we have $\nu = 0$ and $\mu^2 \leq 1$. For $\xi = -1$ we have $\mu = 0$ and $\nu^2 \leq 1$. For any $\xi^2 < 1$, putting $\sigma = 0$ we can find the geometrical form

FIG. 25. Representation of the orbifold for the C_∞ group action on $\Sigma = S^2 \times S^2$ in non-polynomial variables $e_1 = \arccos \xi$, $e_2 = \arccos(\mu + \nu)$, $e_3 = \arccos(\mu - \nu)$. Only one part of the orbifold is shown.

of the border of each part of the orbifold in 3D- (ξ, μ, ν) -space. The equation for the border has the form

$$\frac{1}{1+\xi} \mu^2 + \frac{1}{1-\xi} \nu^2 = \frac{1}{2}. \quad (\text{A3})$$

So any $\xi = \text{const}$ section of one part of the orbifold is an ellipsoid. The complete orbifold may be constructed by identifying the surfaces of two 3D-bodies corresponding to $\sigma \geq 0$ and $\sigma \leq 0$ parts of the orbifold.

To precise the topological structure of the orbifold it is necessary to use some additional information about topology of three dimensional manifolds (Fomenko, 1983; Thurston, 1969).

Every 3-manifold can be obtained from two handlebodies (of some genus) by gluing their boundaries together. Such a representation is called a Heegard decomposition. It is not unique and defined by number g (the genus of the boundary of two auxiliary manifolds) and by mapping of the boundaries. It is known that the only 3-manifold, possessing the Heegard decomposition of genus 0 is the 3-D sphere.

The constructed above orbifold is given just in the form of the Heegard decomposition of genus 0, thus the topological structure of the orbifold is the three dimensional sphere S_3 ($\Sigma|C_\infty \sim S_3$) with four marked points corresponding to 0-D stratum. This result agrees perfectly with the result of analytical treatment made in II C.

Using non-polynomial transformation of the variables ξ, μ, ν to new ones of the type

$$\arccos \xi, \arccos(\mu + \nu), \arccos(\mu - \nu) \quad (\text{A4})$$

we can represent the orbifold in more simple geometrical way (as two tetrahedra with identified surfaces) but with the same topological properties (see Fig.25). These non-polynomial variables may be interpreted as angles in the $(x = j+k, y = j-k)$ representation characterizing angles between x and y and the symmetry axis.

FIG. 26. Representation of energy levels of the Hamiltonian $H = 2\mu - \nu$ on the C_∞ orbifold. Only one part ($\sigma \geq 0$) of the orbifold is shown.

For the group C_∞ an example of the simplest effective invariant operator may be written in the form of the linear combination of the invariant polynomials

$$H = c_1 \xi + c_2 \mu + c_3 \nu. \quad (\text{A5})$$

To get the generic Hamiltonian it is necessary to choose the coefficients c_i in such a way that any section of the orbifold includes at most one critical orbit. Let chose one particular form

$$H = 2\mu - \nu. \quad (\text{A6})$$

We have four sections of the orbifold which go through the critical orbits and three connected components of the generic sections. They are denoted by letters according to their energy: a: $E = -2$; b: $-1 > E > -2$; c: $E = -1$; d: $1 > E > -1$; e: $E = 1$; f: $2 > E > 1$; g: $E = 2$. Four sections a, c, d, g corresponding to energies of critical orbits are shown in the Fig.26.

3. $C_{\infty v}$ invariant Hamiltonian

Orbifolds for other one dimensional Lie subgroups of $O(3)$, $G = C_{\infty v}, C_{\infty h}, D_\infty, D_{\infty h}$, can be constructed from that for the C_∞ group. It is sufficient to take into account the action of G/C_∞ on invariant polynomials given by Table VII and to note that the action on orbits is equivalent to the action on invariant polynomials.

The orbifold for the $C_{\infty v}$ subgroup results from that of the C_∞ one by noting that the σ_v operation relates two orbits which belong to the same part of the C_∞ orbifold characterized by a given sign of the σ invariant. So it is sufficient to take the $\mu > 0$ parts of both 3D-bodies corresponding to different signs of σ . To proper represent the $C_{\infty v}$ orbifold we use the ξ, ν, μ^2 variables which are

FIG. 27. Orbifold for $C_{\infty v}$ group action on Σ .

the invariant polynomials for the $C_{\infty v}$ group. In such a variables each $\xi = \text{const}$, $\xi \neq \pm 1$, section of the orbifold is a parabola. The orbifold is shown in Fig.27.

It should be noted that the identification of points on the surfaces of C_{∞} orbifold results in the identification of the C_1 points on the surfaces of two parts of $C_{\infty v}$ orbifold. All points on the surfaces which do not belong to the C_s stratum should be identified by pairs. At the same time the C_s invariant orbits lying on $\sigma \geq 0$ and on $\sigma \leq 0$ parts of the $C_{\infty v}$ orbifold at $\mu^2 = 0$, $\sigma \neq 0$ are different. This is due to the fact that they correspond to $\sigma \neq 0$.

We can again use nonlinear transformation of variables to reach more simple geometrical form of the orbifold. In new variables

$$\arccos \xi, \arccos(\sqrt{\mu^2} + \nu), \arccos(\sqrt{\mu^2} - \nu) \quad (\text{A7})$$

each part of the orbifold is a tetrahedron shown in Fig.28. These non-polynomial variables may be again interpreted as angles in the $(x = j + k, y = j - k)$ representation characterizing angles between x and y and the symmetry axis. From the topological point of view the orbifold is a 3D-ball, B_3 , with one marked point (C_{∞} orbit) inside and with S^2 surface which includes 2D-stratum (C_s) plus two isolated points ($C_{\infty v}$ orbits). The schematic topological structure of the orbifold is shown in Fig.29. It is useful to note that submanifold formed by both C_s and $C_{\infty v}$ strata is a closed 3D-manifold invariant with respect to the C_s subgroup of the $C_{\infty v}$ invariance group. Its topological structure is the suspension of the 2D-torus (see Section III F for discussion of the topology of this closed submanifold). This fact is important for detailed classification of $C_{\infty v}$ -invariant Morse-Bott functions.

4. $C_{\infty h}$ invariant Hamiltonian

For the $C_{\infty h}$ subgroup the σ_h operation relates C_{∞} orbits with opposite σ and ν values. In order to have the

FIG. 28. Orbifold for $C_{\infty v}$ group action on Σ represented in non-polynomial variables $k_1 = \arccos \xi$, $k_2 = \arccos(|\mu| + \nu)$, $k_3 = \arccos(|\mu| - \nu)$. Only one part of the orbifold is shown.

FIG. 29. Schematic topological structure of the orbifold for $C_{\infty v}$ group action on Σ .

FIG. 30. Orbifold for $C_{\infty h}$ group action on Σ .

one-to-one correspondence between orbits and invariant polynomial values we must unify in one point of the $C_{\infty h}$ orbifold pairs of orbits of the C_{∞} orbifold according to the rule

$$(\xi, \mu, \nu) = (\xi, \mu, -\nu) \quad (\text{A8})$$

Orbits of C_{∞} having $\nu = 0, \sigma = 0$ are invariant with respect to the $C_{\infty h}$ group. Thus the orbifold for the $C_{\infty h}$ group may be constructed from the C_{∞} one by taking only $\nu \geq 0$ parts of two bodies with identification of all corresponding points on the surfaces. This orbifold is shown in Fig.30.

As soon as invariant polynomial for $C_{\infty h}$ has the form ν^2 rather than ν , it is more meaningful to change the variables and to give the orbifold in ξ, μ, ν^2 variables. In this variables each $\xi = \text{const}$, $\xi \neq 0$, section has the form of a parabola

$$\nu^2 = -\frac{1-\xi}{1+\xi} \mu^2 + \frac{1-\xi}{2}. \quad (\text{A9})$$

One should remark that the geometrical form of the $C_{\infty h}$ orbifold in ξ, μ, ν^2 variables is the same as the geometrical form of the $C_{\infty v}$ orbifold in ξ, μ^2, ν variables (whereas the system of strata is completely different in two cases).

We can use more complicated non-polynomial variables

$$\arccos \xi, \arccos(\mu + \sqrt{\nu^2}), \arccos(\mu - \sqrt{\nu^2}) \quad (\text{A10})$$

to reach the simpler geometrical form of the orbifold. It is shown in Fig.31. These non-polynomial variables are again the angles characterizing the mutual positions of x, y and the symmetry axis in the (x, y) representation.

From the topological point of view this orbifold is given in the form of the Heegard decomposition of genus 0. So the $C_{\infty h}$ orbifold is a S_3 manifold with one S_1 marked circle and three marked points: one isolated (C_{∞} orbit) point and two ($C_{\infty h}$ orbits) lying on the S_1 marked circle (formed by C_s, C_i , and $C_{\infty h}$ strata).

FIG. 31. Orbifold for $C_{\infty h}$ group action on Σ represented in non-polynomial variables $t_1 = \arccos \xi$, $t_2 = \arccos(\mu + |\nu|)$, $t_3 = \arccos(\mu - |\nu|)$. Only one part of the orbifold is shown.

FIG. 32. Splitting of the space of C_{∞} invariant polynomial variables ξ, μ, ν into parts with particular signs of D_{∞} auxiliary (numerator) invariants.

$\begin{array}{ c c c } \hline \nu\sigma & \mu\sigma & \mu\nu \\ \hline - & - & + \\ \hline \end{array}$	$\begin{array}{ c c c } \hline \nu\sigma & \mu\sigma & \mu\nu \\ \hline - & + & - \\ \hline \end{array}$	$\begin{array}{ c c c } \hline \nu\sigma & \mu\sigma & \mu\nu \\ \hline + & + & + \\ \hline \end{array}$	$\begin{array}{ c c c } \hline \nu\sigma & \mu\sigma & \mu\nu \\ \hline + & - & - \\ \hline \end{array}$
III ⁺	II ⁺	III ⁻	II ⁻
μ		μ	
IV ⁺	I ⁺	IV ⁻	I ⁻
$\begin{array}{ c c c } \hline \nu\sigma & \mu\sigma & \mu\nu \\ \hline + & - & - \\ \hline \end{array}$	$\begin{array}{ c c c } \hline \nu\sigma & \mu\sigma & \mu\nu \\ \hline + & + & + \\ \hline \end{array}$	$\begin{array}{ c c c } \hline \nu\sigma & \mu\sigma & \mu\nu \\ \hline - & + & - \\ \hline \end{array}$	$\begin{array}{ c c c } \hline \nu\sigma & \mu\sigma & \mu\nu \\ \hline - & - & + \\ \hline \end{array}$
ν		ν	
$\sigma \geq 0$		$\sigma \leq 0$	

We remark again that there are two closed submanifolds formed each by two different strata. One is formed by C_s and $C_{\infty h}$ strata and another by C_i and $C_{\infty h}$ strata. These both manifolds are S_2 spheres from the topological point of view.

5. D_{∞} invariant Hamiltonian

In the case of the D_{∞} symmetry the action of the G/C_{∞} group on the C_{∞} orbifold form larger orbits by relating orbits (ξ, μ, ν) and $(\xi, -\mu, -\nu)$ with opposite σ values. To construct the orbifold for the D_{∞} group we first subdivide the C_{∞} orbifold into parts with semidefinite signs of the D_{∞} group numerator invariants $(\nu\sigma, \mu\sigma, \mu\nu)$. Such a splitting of the ξ, μ, ν space of C_{∞} invariant polynomials into parts with specific signs of the D_{∞} numerator invariants is shown in Fig.32.

Taking into account the action of the C_2 operation on

FIG. 33. Orbifold for D_∞ group action on Σ represented in polynomial variables ξ , μ^2 , ν^2 . The identification of faces, edges, and vortexes of four bodies is given in A11d.

FIG. 34. Orbifold for $D_{\infty h}$ group action on Σ represented in polynomial variables ξ , μ^2 , ν^2 .

FIG. 35. Schematic topological representation of the orbifold for $D_{\infty h}$ group action on Σ .

C_∞ orbits, the D_∞ orbifold may be represented as four 3D-bodies shown in Fig.33 in D_∞ invariant polynomial variables ξ , μ^2 , ν^2 with the following identification of faces, edges and vortexes:

$$A_1 B_1 C_1 D_1 = a_1 b_1 c_1 d_1, \quad (A11a)$$

$$A_4 B_4 C_4 D_4 = a_4 b_4 c_4 d_4,$$

$$A_1 B_1 C_1 = A_4 B_4 C_4, \quad A_1 C_1 D_1 = a_4 c_4 d_4, \quad (A11b)$$

$$A_4 C_4 D_4 = a_1 c_1 d_1, \quad a_1 b_1 c_1 = a_4 b_4 c_4,$$

$$A_1 C_1 = a_1 c_1 = A_4 C_4 = a_4 c_4, \quad (A11c)$$

$$A_1 B_1 = A_4 B_4 = a_1 b_1 = a_4 b_4,$$

$$B_1 C_1 = B_4 C_4 = b_1 c_1 = b_4 c_4,$$

$$A_1 D_1 = a_4 d_4 = A_4 D_4 = a_1 d_1,$$

$$C_1 D_1 = c_4 d_4 = C_4 D_4 = c_1 d_1,$$

$$A_1 = A_4 = a_1 = a_4, \quad B_1 = B_4 = b_1 = b_4, \quad (A11d)$$

$$C_1 = C_4 = c_1 = c_4, \quad D_1 = D_4 = d_1 = d_4.$$

In fact we have constructed the representation of the orbifold as a simplicial complex. It consists of four 3D-simplexes, six 2D-simplexes, five 1D-simplexes and four 0D-simplexes. The Euler-Poincaré characteristics of this complex differs from zero

$$\sum (-1)^p a^p = 4 - 5 + 6 - 4 = 1. \quad (A12)$$

Here a^p is the number of p -dimensional simplexes. As it is shown in II C, the orbifold is the suspension(RP_2).

6. $D_{\infty h}$ invariant Hamiltonian

To go from the D_∞ orbifold to the $D_{\infty h}$ one it is sufficient to consider the action of σ_h operation on the D_∞ orbifold. As soon as the σ_h operation change simultaneously signs of ν and σ it relates orbits characterized by $(\nu\sigma > 0, \mu\sigma > 0, \mu\nu > 0)$ and $(\nu\sigma > 0, \mu\sigma < 0, \mu\nu < 0)$ and in a similar way orbits characterized by $(\nu\sigma < 0, \mu\sigma < 0, \mu\nu > 0)$ and $(\nu\sigma < 0, \mu\sigma > 0, \mu\nu < 0)$. As a consequence, for the $D_{\infty h}$ orbifold we have only one body instead of each pair of bodies with the same geometrical form. The $D_{\infty h}$ orbifold is shown in Fig.34.

It consists of two bodies. The points on two pairs of faces must be identified whereas the third pair of faces (formed by the C_s stratum) must not be identified. From the topological point of view the $D_{\infty h}$ orbifold is equivalent to a 3D-ball. The border is formed by $C_s, C_{2v}, C_{2h}, C_{\infty v}$ strata. Inside the ball there are $C_i, C_s, C_{\infty h}$, and the generic C_1 strata. The schematic topological view of the $D_{\infty h}$ orbifold is given in Fig.35. Several closed subspaces formed by different strata are clearly seen in Fig.35. It is important to verify that the Morse-Bott inequalities are satisfied on all these subspaces.

APPENDIX B: MOLIER FUNCTIONS FOR POINT GROUP INVARIANTS.

This appendix deals with technical question: How to describe the system of invariant polynomials on Σ manifold under the presence of a nonlinear action of the symmetry group. The schematic answer on this question was formulated in Section III G. Particular example of the symmetry group G_4 for the hydrogen atom on orthogonal electric and magnetic fields was treated in more details in Section V D. Group G_4 has interesting physical meaning because it includes symmetry transformations which includes both spatial and time reversal operations but it is Abelian and this simplifies significantly the construction of the Molien function for invariants. Below we explain on several examples of point symmetry groups with increasing complexity the procedure of the Molien function construction.

The construction of invariant functions on the Σ manifold is based on the preliminary construction of the integrity basis on the 6 dimensional space where the action of the symmetry group of the problem is linear. The Molien function and the invariants themselves for the 6 dimensional space $x+y$ or $k+j$ may be found from known expressions for Molien functions and integrity bases for irreducible representations. Next step includes the restriction of the polynomial algebra on the submanifold Σ of the 6D-space. The general procedure of the restriction of the polynomial ring defined on the manifold to the submanifold was outlined in subsubsection II B 1. The submanifold Σ is defined in the 6 dimensional space $x+y$ by the polynomial equations $x^2 = 1/2$, $y^2 = 1/2$. If the point symmetry group does not include improper rotations (inversion or reflections) these polynomials may always be considered as denominator invariants. In such a case we just eliminate them from the integrity basis constructed for the 6D-space and the resulting integrity basis gives the basis for the 4D submanifold.

For point groups which are not the subgroups of $SO(3)$ we start with the consideration of the similar problem for the proper rotation subgroup and after that take into account the effect of improper symmetry elements working directly on the 4D-submanifold Σ .

1. C_1 group

This trivial case is useful to demonstrate how to take into account the restriction of the polynomial ring on the submanifold.

We work in $x+y$ representation. On the 6D-space there are six basic invariants x_i, y_i ($i = 1, 2, 3$) and the Molien function for invariants has a trivial form

$$M_{C_1} = \frac{1}{(1-\lambda)^6} \quad (B1)$$

The ring of the invariant polynomials on the 6D-space $\mathcal{P}_6^{C_1}$ is the ring of all polynomials

$$\mathcal{P}_6^{C_1} = P[x_1, x_2, x_3, y_1, y_2, y_3]. \quad (B2)$$

To restrict the polynomial ring on the submanifold

$$\theta_5 = x_1^2 + x_2^2 + x_3^2 = 1/2, \quad (B3a)$$

$$\theta_6 = y_1^2 + y_2^2 + y_3^2 = 1/2 \quad (B3b)$$

we are obliged to introduce two second order polynomials, θ_5, θ_6 given by (B3) as denominator invariants. This may be done by multiplying both the numerator and denominator of the Molien function (B1) by $(1+\lambda)^2$. The new form of the Molien function

$$M_{C_1} = \frac{1+2\lambda+\lambda^2}{(1-\lambda)^4(1-\lambda^2)^2}. \quad (B4)$$

corresponds now to another description of the ring of invariants $\mathcal{P}_6^{C_1}$ which is considered as a free module

$$\mathcal{P}_6^{C_1} = P[x_1, x_2, \theta_5, y_1, y_2, \theta_6] \bullet (1, x_3)(1, y_3). \quad (B5)$$

with four auxiliary invariants $\varphi_1 = 1$, $\varphi_2 = x_3$, $\varphi_3 = y_3$, $\varphi_4 = x_3 y_3$. We use the notation $(a, b)(c, d) = (ac, ad, bc, bd)$ to show that four numerator invariants are represented as product of more simple terms. Having the form (B4) of the Molien function and the form (B5) of the module of invariant functions it is easy to make the restriction to the submanifold Σ . We just eliminate two denominator invariants, θ_5, θ_6 , corresponding to the equation defining Σ . The resulting Molien function and the module of invariants on Σ are written as follows:

$$M_{C_1}|_{\Sigma} = \frac{1+2\lambda+\lambda^2}{(1-\lambda)^4}, \quad (B6a)$$

$$\mathcal{P}_6^{C_1}|_{\Sigma} = P[x_1, x_2, y_1, y_2] \bullet (1, x_3)(1, y_3). \quad (B6b)$$

The choice of basic and auxiliary invariants is ambiguous and that proposed here is just an example. The important point is that the integrity basis may be constructed which includes four numerator invariants (including 1) and four denominator invariants.

To find now the integrity basis in $j+k$ representation we can simply transform invariants from x, y to j, k representation.

2. C_2 point group

Let take x_3 and y_3 to coincide with the C_2 axis. In such a case x_1, x_2, y_1, y_2 transform according to the B representation and x_3, y_3 according to the A representation of the C_2 point group. The Molien function for invariants constructed from 6D reducible representation $4B + 2A$ has the form

$$M_{C_2} = \frac{1+6\lambda^2+\lambda^4}{(1-\lambda^2)^4(1-\lambda)^2}. \quad (B7)$$

The explicit form of the module of invariant functions on 6D-space may be easily given as well:

$$\mathcal{P}_6^{C_2} = P[x_1^2, x_2^2, x_3, y_1^2, y_2^2, y_3] \bullet ((1, x_1 x_2)(1, y_1 y_2), (x_1, x_2)(y_1, y_2)) \quad (\text{B8})$$

There are 6 denominator invariants and 8 numerator invariants. We have in (B8) second degree denominator invariants which may be replaced by invariants defining the submanifold Σ (B3). After such a substitution, to make the restriction on Σ it is sufficient to omit two denominator invariants corresponding to equations defining Σ . The resulting Molien function for invariant polynomials on Σ and the description of the ring of invariant function as a module are as follows:

$$M_{C_2}|_{\Sigma} = \frac{1+6\lambda^2+\lambda^4}{(1-\lambda^2)^2(1-\lambda)^2}. \quad (\text{B9})$$

$$\mathcal{P}^{C_2}|_{\Sigma} = P[x_1^2, x_3, y_1^2, y_3] \bullet ((1, x_1 x_2)(1, y_1 y_2), (x_1, x_2)(y_1, y_2)) \quad (\text{B10})$$

To find the integrity basis in the $j+k$ representation we can use again the transformation from x, y to j, k representation.

3. C_i point group

For point groups which are not the subgroups of $SO(3)$ the procedure of constructing the Molien function for invariants on Σ and the integrity basis is slightly different. We start with the consideration of the similar problem for the proper rotation subgroup of the point group. There are two groups C_i (or in other notation S_2) and C_s which have no nontrivial rotational subgroups. So we use them to illustrate the construction of invariant functions for these cases. The C_i group includes only one nontrivial symmetry operation, inversion. Its action on x, y variables corresponds to interchange $x \leftrightarrow y$. Taking this action into account it is easy to make the transformation of the C_1 invariant denominator and numerator polynomials (forming the module of invariant polynomials on Σ) into form with irreducible transformation properties with respect to the C_i group.

$$\mathcal{P}^{C_i}|_{\Sigma} = P[x_1 + y_1, x_1 - y_1, x_2 + y_2, x_2 - y_2] \bullet ((1, x_3 + y_3)(1, x_3 - y_3)) \quad (\text{B11})$$

This form of the module of C_1 invariant function on Σ is well adapted to transformation to the module of C_i invariant functions. First we change the denominator invariants $(x_1 - y_1)$ and $(x_2 - y_2)$ into $(x_1 - y_1)^2 \sim x_1 y_1$ and $(x_2 - y_2)^2 \sim x_2 y_2$ which are both C_1 and C_i invariants. This may be achieved by multiplying the numerator and denominator of the Molien function by $(1 + \lambda)^2$. The module of C_1 invariant function on Σ in such a case will include 16 auxiliary (numerator) invariants but among them only 8 are C_i invariant. The resulting Molien function and the module of C_i invariants on Σ are written as follows:

$$M_{C_i}|_{\Sigma} = \frac{1+\lambda+4\lambda^2+\lambda^3+\lambda^4}{(1-\lambda^2)^2(1-\lambda)^2} \quad (\text{B12a})$$

$$\mathcal{P}^{C_i}|_{\Sigma} = P[x_1 + y_1, x_2 + y_2, x_1 y_1, x_2 y_2] \bullet (1, \varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6, \varphi_7), \quad (\text{B12b})$$

$$\varphi_1 = x_3 + y_3, \quad \varphi_2 = x_3 y_3, \quad (\text{B12c})$$

$$\varphi_3 = (x_1 - y_1)(x_2 - y_2), \quad \varphi_4 = \varphi_1 \varphi_3, \quad (\text{B12d})$$

$$\varphi_5 = \varphi_2 \varphi_3, \quad \varphi_6 = (x_3 - y_3)(x_1 - y_1), \quad (\text{B12e})$$

$$\varphi_7 = (x_3 - y_3)(x_2 - y_2). \quad (\text{B12f})$$

4. C_s point group

The construction of the module of C_s invariant functions on Σ very similar to the realized above construction for the C_i invariants. The only difference is that the action of the C_s nontrivial operation (reflection in the symmetry plane) is now different from the action of the inversion for the C_i group. Let suppose the symmetry plane to be orthogonal to x_3 (y_3) axes. In such a case $(x_1 - y_1)$ and $(x_2 - y_2)$ are symmetrical with respect to the C_s group whereas $(x_1 + y_1)$ and $(x_2 + y_2)$ are antisymmetrical. Taking this into account the Molien function and the module of C_s invariants on Σ are written immediately as follows:

$$M_{C_s}|_{\Sigma} = \frac{1+\lambda+4\lambda^2+\lambda^3+\lambda^4}{(1-\lambda^2)^2(1-\lambda)^2} \quad (\text{B13a})$$

$$\mathcal{P}^{C_s}|_{\Sigma} = P[x_1 - y_1, x_2 - y_2, x_1 y_1, x_2 y_2] \bullet (1, \varphi_1, \varphi_2, \varphi_3, \varphi_4, \varphi_5, \varphi_6, \varphi_7), \quad (\text{B13b})$$

$$\varphi_1 = x_3 + y_3, \quad \varphi_2 = x_3 y_3, \quad (\text{B13c})$$

$$\varphi_3 = (x_1 + y_1)(x_2 + y_2), \quad \varphi_4 = \varphi_1 \varphi_3, \quad (\text{B13d})$$

$$\varphi_5 = \varphi_2 \varphi_3, \quad \varphi_6 = (x_3 - y_3)(x_1 + y_1), \quad (\text{B13e})$$

$$\varphi_7 = (x_3 - y_3)(x_2 + y_2). \quad (\text{B13f})$$

5. C_{2v} point group

For the point group C_{2v} which is not a subgroups of $SO(3)$ we start again with the consideration of the similar problem for the proper rotation subgroup C_2 . We can take the Molien function for C_2 invariant and integrity basis for the C_2 group as the initial point. All invariants of C_2 span invariants and pseudo-invariants of C_{2v} ($A_1 + A_2$ representations). So we make first the linear transformation of numerator and denominator invariants for the C_2 group resulting in a new set of C_2 invariants which are at the same time either of A_1 or of A_2 type with respect to the C_{2v} group. This linear transformation does not change the form of the Molien function. It is of the form (B9) found for the C_2 invariants on Σ . However

this transformation changes the basis of the module of C_2 invariant functions on Σ .

To find proper linear combinations which transform according irreducible representation of the C_{2v} group we take into account the fact that two symmetry operations (σ_{13}, σ_{23}) which belong to C_{2v} group but do not belong to C_2 group may be represented as products of inversion and the C_2 rotation around the axis orthogonal to the reflection plane. We note again that the action of the inversion results in the interchange of x_i with y_i and the action of σ_{13}, σ_{23} on x_i, y_i may be represented as follows:

$$\sigma_{13}x_j \leftrightarrow -y_j, (j = 1, 3); \quad \sigma_{13}x_2 \leftrightarrow y_2, \quad (B14a)$$

$$\sigma_{23}x_j \leftrightarrow -y_j, (j = 2, 3); \quad \sigma_{23}x_1 \leftrightarrow y_1. \quad (B14b)$$

So, instead of four denominator invariants (x_3, y_3, x_1^2, y_1^2) we should take two linear combinations $\theta_{1s} = (x_1^2 + y_1^2)$ and $\theta_{2s} = (x_3 - y_3)$ which are invariant with respect to C_{2v} and two combinations $\theta_{1a} = (x_1^2 - y_1^2)$ and $\theta_{2a} = (x_3 + y_3)$ which are pseudo-invariants of type A_2 with respect to C_{2v} . In a similar way we form new numerator invariants. Six numerator invariants are of type A_1 with respect to C_{2v} : $1, \varphi_{1s} = x_1x_2 - y_1y_2, \varphi_{2s} = x_1y_1, \varphi_{3s} = x_2y_2, \varphi_{4s} = x_1y_2 - x_2y_1, \varphi_{5s} = x_1x_2y_1y_2$. There are equally two numerator C_2 invariants which are pseudo-invariants of the type A_2 with respect to C_{2v} : $\varphi_{1a} = x_1y_2 + x_2y_1, \varphi_{2a} = x_1x_2 + y_1y_2$. The module of C_2 invariant functions of Σ is represented now as

$$\mathcal{P}^{C_2}|_{\Sigma} = \quad (B15)$$

$$P[\theta_{1s}, \theta_{2s}, \theta_{1a}, \theta_{2a}] \bullet (1, \varphi_{2s}, \varphi_{3s}, \varphi_{4s}, \varphi_{5s}, \varphi_{6s}, \varphi_{1a}, \varphi_{2a}).$$

Now we can transform the basis of the module of the C_2 invariant functions in such a way that new denominator invariants become C_{2v} invariants rather than pseudo-invariants. To do that it is sufficient to multiply the numerator and denominator of the Molien function by $(1 + \lambda)(1 + \lambda^2)$. This action corresponds simply to the substitution of two C_2 denominators invariants θ_{1a} and θ_{2a} by their squares which are C_{2v} invariants. The new representation of the module of the C_2 invariants on Σ takes the form

$$\mathcal{P}^{C_2}|_{\Sigma} = P[\theta_{1s}, \theta_{2s}, (\theta_{1a})^2, (\theta_{2a})^2] \bullet \quad (B16)$$

$$\bullet (1, \varphi_{2s}, \varphi_{3s}, \varphi_{4s}, \varphi_{5s}, \varphi_{6s}, \varphi_{1a}, \varphi_{2a})(1, \theta_{1a})(1, \theta_{2a})$$

To make the restriction to C_{2v} invariant functions it is sufficient now to take only those numerator invariant which are C_{2v} invariants. The representation of the module of C_{2v} invariant functions on Σ takes the form

$$\mathcal{P}^{C_{2v}}|_{\Sigma} = P[\theta_{1s}, \theta_{2s}, \theta_{1a}^2, \theta_{2a}^2] \bullet \quad (B17)$$

$$\bullet ((1, \theta_{1a}\theta_{2a})(1, \sum \varphi_{is}), (\theta_{1a}, \theta_{2a})(\sum \varphi_{ia}))$$

including 16 numerator invariants. The corresponding Molien function has the form (B18)

$$M_{C_{2v}}|_{\Sigma} = \frac{1+4\lambda^2+3\lambda^4+3\lambda^3+4\lambda^5+\lambda^7}{(1-\lambda)(1-\lambda^2)^2(1-\lambda^4)} \quad (B18)$$

$$= \frac{1+3\lambda^2+3\lambda^3+\lambda^5}{(1-\lambda)(1-\lambda^2)^3} \quad (B19)$$

which turns out to be reduced to more simpler one (B19) which includes only eight numerator invariants. Construction of the integrity basis corresponding to the reduced form of the Molien function (B19) requires additional analysis because we should find three second order algebraically independent invariants. At the same time the straightforward procedure realized above give one of the possible basis of the module of invariant functions although not a minimal one.

6. D_{3h} group

We begin by constructing the Molien function of D_3 invariants over the 6D space $x+y$. This 6D vector space is the six-dimensional reducible representation of the form $(E + A_2) + (E + A_2)$. The corresponding Molien function is

$$M_{D_3} = \frac{1+2\lambda^4+4\lambda^3+10\lambda^4+4\lambda^5+2\lambda^6+\lambda^8}{(1-\lambda^2)^4(1-\lambda^3)^2} \quad (B20)$$

Its restriction on the Σ subspace has the form

$$M_{D_3}|_{\Sigma} = \frac{1+2\lambda^4+4\lambda^3+10\lambda^4+4\lambda^5+2\lambda^6+\lambda^8}{(1-\lambda^2)^2(1-\lambda^3)^2} \quad (B21)$$

To go now to D_{3h} group we first rewrite the Molien function for the D_3 invariants on Σ using two auxiliary variables λ_s, λ_a instead of one λ . We use subscript to differ the behavior of D_3 invariants with respect to reflection.

First, the Molien function for the D_3 invariants on Σ with two parameters has the form

$$M_{D_3}|_{\Sigma} = \frac{1+2\lambda_s^2+2\lambda_s^3+6\lambda_s^4+2\lambda_s^5+2\lambda_s^6+\lambda_s^8+(2\lambda_a^3+4\lambda_a^4+2\lambda_a^5)}{(1-\lambda_s^2)(1-\lambda_a^2)(1-\lambda_s^3)(1-\lambda_a^3)} \quad (B22)$$

We transform it to new denominator invariants which are at the same time D_{3h} invariants.

$$M_{D_3}|_{\Sigma} = \frac{(1+2\lambda_s^2+2\lambda_s^3+6\lambda_s^4+2\lambda_s^5+2\lambda_s^6+\lambda_s^8)+(2\lambda_a^3+4\lambda_a^4+2\lambda_a^5)}{(1-\lambda_s^2)(1-(\lambda_a^2)^2)(1-\lambda_s^3)(1-(\lambda_a^3)^2)} \times \quad (B23)$$

$$\times (1 + \lambda_a^2)(1 + \lambda_a^3)$$

To pass to D_{3h} invariants one must take only those numerator D_3 invariants which are D_{3h} invariants. The Molien function for D_{3h} invariants is written in the form with the only parameter λ

$$M_{D_{3h}}|_{\Sigma} = \frac{(1+\lambda^5)[1+2\lambda^2+2\lambda^3+6\lambda^4+2\lambda^5+2\lambda^6+\lambda^8]}{(1-\lambda^2)(1-\lambda^4)(1-\lambda^3)(1-\lambda^6)} + \frac{(\lambda^2+\lambda^3)[2\lambda^3+4\lambda^4+2\lambda^5]}{(1-\lambda^2)(1-\lambda^4)(1-\lambda^3)(1-\lambda^6)} \quad (B24)$$

which is equivalent to

$$M_{D_{3h}}|_{\Sigma} = \frac{1+2\lambda^2+2\lambda^3+6\lambda^4+5\lambda^5+8\lambda^6+8\lambda^7+5\lambda^8+6\lambda^9+2\lambda^{10}+2\lambda^{11}+\lambda^{13}}{(1-\lambda^2)(1-\lambda^3)(1-\lambda^4)(1-\lambda^6)} \quad (\text{B25})$$

There are four D_{3h} denominator invariants (degree 2,3,4,6) and 48 numerator invariants. Remark that this is not the simplest form of the Molien function because the numerator may be factorize and $(1+\lambda^2)$ factor may be simultaneously eliminated from numerator and denominator resulting in the reduced form of the Molien function

$$M_{D_{3h}}|_{\Sigma} = \frac{1+\lambda^2+2\lambda^3+5\lambda^4+3\lambda^5+3\lambda^6+5\lambda^7+2\lambda^8+\lambda^9+\lambda^{11}}{(1-\lambda^2)^2(1-\lambda^3)(1-\lambda^6)} \quad (\text{B26})$$

Although the question is open how to construct integrity basis corresponding to this simplified Molien function (B26), the construction of the non-minimal integrity basis corresponding to the form (B25) of the D_{3h} Molien function is straightforward.

To give the explicit form of the integrity basis over the six dimensional space we need the basis for all invariants and covariants over three dimensional space. Instead of x_i and y_i we can use irreducible tensors with respect to D_3 group on each 3D-subspace to construct the integrity basis on Σ of functions invariant with respect to D_3 group action on the 6D-space.

First of all we give the explicit form of D_3 invariant and covariants on three dimensional space which form the basis of the module of polynomials. There are three basic (denominator) invariants

$$x_1^2 + x_2^2, \quad x_3^2, \quad \gamma_3(x) = x_1^3 - 3x_1x_2^2 \quad (\text{B27})$$

and one auxiliary (numerator) invariant

$$x_3\sigma_3(x), \quad \sigma_3(x) = 3x_1^2x_2 - x_2^3 \quad (\text{B28})$$

There are two auxiliary covariants of the type A_2 (degree 1 and 3)

$$x_3, \quad \sigma_3(x) \quad (\text{B29})$$

and four pairs of auxiliary covariants of the type E (degree 1, 2, 2, and 3)

$$\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}, \quad \begin{pmatrix} x_1^2 - x_2^2 \\ -2x_1x_2 \end{pmatrix}, \quad \begin{pmatrix} x_2x_3 \\ -x_1x_3 \end{pmatrix}, \quad (\text{B30a})$$

$$\begin{pmatrix} 2x_1x_2x_3 \\ (x_1^2 - x_2^2)x_3 \end{pmatrix} \quad (\text{B30b})$$

Taking into account the form of these invariants and covariants for 3D x and 3D y spaces and the expression for the Molien function (B21) for D_3 invariants on Σ we can write the following representation for the module of D_3 invariant functions of Σ .

$$\mathcal{P}^{D_3}|_{\Sigma} = P[x_3^2, \gamma_3(x), y_3^2, \gamma_3(y)] \bullet (1, \varphi_1, \dots, \varphi_{23}) \quad (\text{B31})$$

There are 24 (including 1) numerator invariants. They are listed below in the form which shows clearly that they are simply invariants produced by coupling x and y covariants

$$\varphi_1 = x_3\sigma_3(x), \quad \varphi_2 = y_3\sigma_3(y), \quad (\text{B32a})$$

$$\varphi_3 = x_3y_3\sigma_3(x)\sigma_3(y), \quad (\text{B32b})$$

$$\varphi_4 = x_3y_3, \quad \varphi_5 = x_3y_2\sigma(y), \quad (\text{B32c})$$

$$\varphi_6 = y_3x_2\sigma(x), \quad \varphi_7 = x_2\sigma(x)y_2\sigma(y) \quad (\text{B32d})$$

$$\varphi_8 = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix}, \quad (\text{B32e})$$

$$\varphi_9 = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \begin{pmatrix} y_1^2 - y_2^2 \\ -2y_1y_2 \end{pmatrix}, \quad (\text{B32f})$$

$$\varphi_{10} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \begin{pmatrix} y_2y_3 \\ -y_1y_3 \end{pmatrix}, \quad (\text{B32g})$$

$$\varphi_{11} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \begin{pmatrix} 2y_1y_2y_3 \\ (y_1^2 - y_2^2)y_3 \end{pmatrix} \quad (\text{B32h})$$

$$\varphi_{12} = \begin{pmatrix} x_1^2 - x_2^2 \\ -2x_1x_2 \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix}, \quad (\text{B32i})$$

$$\varphi_{13} = \begin{pmatrix} x_1^2 - x_2^2 \\ -2x_1x_2 \end{pmatrix} \begin{pmatrix} y_1^2 - y_2^2 \\ -2y_1y_2 \end{pmatrix}, \quad (\text{B32j})$$

$$\varphi_{14} = \begin{pmatrix} x_1^2 - x_2^2 \\ -2x_1x_2 \end{pmatrix} \begin{pmatrix} y_2y_3 \\ -y_1y_3 \end{pmatrix}, \quad (\text{B32k})$$

$$\varphi_{15} = \begin{pmatrix} x_1^2 - x_2^2 \\ -2x_1x_2 \end{pmatrix} \begin{pmatrix} 2y_1y_2y_3 \\ (y_1^2 - y_2^2)y_3 \end{pmatrix} \quad (\text{B32l})$$

$$\varphi_{16} = \begin{pmatrix} x_2x_3 \\ -x_1x_3 \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix}, \quad (\text{B32m})$$

$$\varphi_{17} = \begin{pmatrix} x_2x_3 \\ -x_1x_3 \end{pmatrix} \begin{pmatrix} y_1^2 - y_2^2 \\ -2y_1y_2 \end{pmatrix}, \quad (\text{B32n})$$

$$\varphi_{18} = \begin{pmatrix} x_2x_3 \\ -x_1x_3 \end{pmatrix} \begin{pmatrix} y_2y_3 \\ -y_1y_3 \end{pmatrix}, \quad (\text{B32o})$$

$$\varphi_{19} = \begin{pmatrix} x_2x_3 \\ -x_1x_3 \end{pmatrix} \begin{pmatrix} 2y_1y_2y_3 \\ (y_1^2 - y_2^2)y_3 \end{pmatrix} \quad (\text{B32p})$$

$$\varphi_{20} = \begin{pmatrix} 2x_1x_2x_3 \\ (x_1^2 - x_2^2)x_3 \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix}, \quad (\text{B32q})$$

$$\varphi_{21} = \begin{pmatrix} 2x_1x_2x_3 \\ (x_1^2 - x_2^2)x_3 \end{pmatrix} \begin{pmatrix} y_1^2 - y_2^2 \\ -2y_1y_2 \end{pmatrix}, \quad (\text{B32r})$$

$$\varphi_{22} = \begin{pmatrix} 2x_1x_2x_3 \\ (x_1^2 - x_2^2)x_3 \end{pmatrix} \begin{pmatrix} y_2y_3 \\ -y_1y_3 \end{pmatrix}, \quad (\text{B32s})$$

$$\varphi_{23} = \begin{pmatrix} 2x_1x_2x_3 \\ (x_1^2 - x_2^2)x_3 \end{pmatrix} \begin{pmatrix} 2y_1y_2y_3 \\ (y_1^2 - y_2^2)y_3 \end{pmatrix} \quad (\text{B32t})$$

we change the basis of the module of D_3 invariant functions in such a way that all invariants become invariants or pseudo-invariants for the D_{3h} group. To do that it is sufficient to form simple linear combinations of denominator and numerator invariants used in (B31). We remark that the action of the σ_h operation which should be added to go from D_3 group to D_{3h} one is given by

$$\sigma_h x_j \leftrightarrow -y_j, \quad (j = 1, 2); \quad \sigma_h x_3 \leftrightarrow y_3 \quad (\text{B33})$$

The new representation of the module of D_3 invariant functions corresponding to the Molien function (B22) with two parameters is as follows:

$$\mathcal{P}^{D_3}|_{\Sigma} = P[\theta_{1s}, \theta_{2s}, \theta_{1a}, \theta_{2a}] \bullet \quad (\text{B34a})$$

$$\bullet (1, \varphi_{1s}, \dots, \varphi_{15s}, \varphi_{1a}, \dots, \varphi_{8a}),$$

$$\theta_{1s} = x_3^2 + y_3^2, \quad \theta_{2s} = \gamma_3(x) - \gamma_3(y), \quad (\text{B34b})$$

$$\theta_{1a} = x_3^2 - y_3^2, \quad \theta_{2a} = \gamma_3(x) + \gamma_3(y), \quad (\text{B34c})$$

$$\varphi_{1s} = \varphi_1 - \varphi_2, \quad \varphi_{2s} = \varphi_5 + \varphi_6, \quad (\text{B34d})$$

$$\varphi_{3s} = \varphi_9 - \varphi_{12}, \quad \varphi_{4s} = \varphi_{10} - \varphi_{16}, \quad (\text{B34e})$$

$$\varphi_{5s} = \varphi_{11} + \varphi_{20}, \quad \varphi_{6s} = \varphi_{14} + \varphi_{17}, \quad (\text{B34f})$$

$$\varphi_{7s} = \varphi_{15} - \varphi_{21}, \quad \varphi_{8s} = \varphi_{19} - \varphi_{22}, \quad (\text{B34g})$$

$$\varphi_{9s} = \varphi_3, \quad \varphi_{10s} = \varphi_4, \quad (\text{B34h})$$

$$\varphi_{11s} = \varphi_7, \quad \varphi_{12s} = \varphi_8, \quad (\text{B34i})$$

$$\varphi_{13s} = \varphi_{13}, \quad \varphi_{14s} = \varphi_{18}, \quad \varphi_{15s} = \varphi_{23}, \quad (\text{B34j})$$

$$\varphi_{1a} = \varphi_1 + \varphi_2, \quad \varphi_{2a} = \varphi_5 - \varphi_6, \quad (\text{B34k})$$

$$\varphi_{3a} = \varphi_9 + \varphi_{12}, \quad \varphi_{4a} = \varphi_{10} + \varphi_{16}, \quad (\text{B34l})$$

$$\varphi_{5a} = \varphi_{11} - \varphi_{20}, \quad \varphi_{6a} = \varphi_{14} - \varphi_{17}, \quad (\text{B34m})$$

$$\varphi_{7a} = \varphi_{15} + \varphi_{21}, \quad \varphi_{8a} = \varphi_{19} + \varphi_{22} \quad (\text{B34n})$$

We change now two denominator invariants θ_{1a}, θ_{2a} into $(\theta_{1a})^2, (\theta_{2a})^2$ which are D_{3h} invariants. This results in increasing the number of numerator D_3 invariants four times. But we are interested only in those numerator invariants which are D_{3h} invariants as well. There are 48 such invariants which corresponds the the form (B25) of the Molien function. The structure of the module of D_{3h} invariant functions on Σ may be now given explicitly

$$\mathcal{P}^{D_3}|_{\Sigma} = P[\theta_{1s}, \theta_{2s}, (\theta_{1a})^2, (\theta_{2a})^2] \bullet \quad (\text{B35})$$

$$\bullet ((1, \theta_{1a}\theta_{2a})(1, \varphi_{1s}, \dots, \varphi_{15s}), (\theta_{1a}, \theta_{2a})(\varphi_{1a}, \dots, \varphi_{8a})).$$

There are four denominator invariants and 48 numerator invariants which may be reconstructed from (B32, B34). Apparently, the smaller integrity basis with only 24 numerator invariants may be found as indicated the form (B26) of the Molien function.

7. T_d point group

To construct the Molien function for the T_d group invariants on Σ we use exactly the same procedure as for the D_{3h} group but we start now from the T group in $(x + y)$ representation. The Molien function for the invariants of T group on Σ has the form

$$M_T|_{\Sigma} = \frac{(1+\lambda^6)^2 + 2(\lambda^2 + \lambda^4)^2 + (\lambda + \lambda^2 + 2\lambda^3 + \lambda^4 + \lambda^5)^2}{(1-\lambda^3)^2(1-\lambda^4)^2}. \quad (\text{B36})$$

More detailed form of the Molien function with two parameters may be given after the transformation of the T invariants into the form irreducible with respect to T_d (A_1

or A_2 symmetry types with respect to T_d). We use below λ_s for those T -invariants which are at the same time the T_d invariants and λ_a for those T -invariants which are pseudo-invariants (of the A_2 type) of the T_d group.

$$M_T|_{\Sigma} = \quad (\text{B37})$$

$$\frac{(1+\lambda_s^2+\lambda_s^3+5\lambda_s^4+3\lambda_s^5+8\lambda_s^6+3\lambda_s^7+5\lambda_s^8+\lambda_s^9+\lambda_s^{10}+\lambda_s^{12})}{(1-\lambda_s^3)(1-\lambda_s^4)(1-\lambda_s^8)} + \frac{(\lambda_a^3+2\lambda_a^4+3\lambda_a^5+6\lambda_a^6+3\lambda_a^7+2\lambda_a^8+\lambda_a^9)}{(1-\lambda_s^3)(1-\lambda_s^4)(1-\lambda_s^8)}.$$

Now to form the Molien function for the T_d invariant on Σ we multiply both numerator and denominator by $(1+\lambda_a^3)(1+\lambda_a^4)$ and take in numerator only those terms which are T_d invariant

$$M_{T_d}|_{\Sigma} = \quad (\text{B38})$$

$$\frac{(1+(\lambda_a^3\lambda_a^4))(1+\lambda_s^2+\lambda_s^3+5\lambda_s^4+3\lambda_s^5+8\lambda_s^6+3\lambda_s^7+5\lambda_s^8+\lambda_s^9+\lambda_s^{10}+\lambda_s^{12})}{(1-\lambda_s^3)(1-(\lambda_a^3)^2)(1-\lambda_s^4)(1-(\lambda_a^4)^2)} + \frac{(\lambda_a^3+\lambda_a^4)(\lambda_a^3+2\lambda_a^4+3\lambda_a^5+6\lambda_a^6+3\lambda_a^7+2\lambda_a^8+\lambda_a^9)}{(1-\lambda_s^3)(1-(\lambda_a^3)^2)(1-\lambda_s^4)(1-(\lambda_a^4)^2)}.$$

The total number of numerator invariants now is 96. If we will use only one auxiliary parameter λ we can simplify considerably the Molien function for T_d invariants. The formula (B38) becomes

$$M_{T_d}|_{\Sigma} = \quad (\text{B39})$$

$$\frac{(1+\lambda^2)(1+\lambda^3)(1+\lambda^4)(1+4\lambda^4+2\lambda^5+4\lambda^6+\lambda^{10})}{(1-\lambda^3)(1-\lambda^6)(1-\lambda^4)(1-\lambda^8)} = \frac{1+4\lambda^4+2\lambda^5+4\lambda^6+\lambda^{10}}{(1-\lambda^3)^2(1-\lambda^2)(1-\lambda^4)}. \quad (\text{B40})$$

The last simplified form (B40) of the Molien function for the T_d invariants on Σ seems to be rather reasonable. Probably it gives the minimal basis of denominator and numerator invariants on Σ . If the integrity basis corresponding to this simplified form (B40) exists it may be used in some applications. The number of auxiliary invariants (12) is not enormous. The initial form (B39) of the integrity basis including 96 numerator invariants is not encouraging at all.

TABLE XXVII. Strata and orbits in the action of C_1 on Σ .

Stabilizer	gc	dim.	number	nature
1	g	4	∞^4	1

TABLE XXVIII. Strata and orbits in the action of C_n ($n \geq 2$) on Σ .

Stabilizer	gc	dim.	number	nature
C_n	c	0	4	1
1	g	4	∞^4	n

APPENDIX C: STRATA AND ORBITS FOR POINT GROUPS.

We gave in Section III H strata and orbits in the action on Σ of three point groups C_{2v} , D_{3h} , and T_d . This choice is due to the fact that among polyatomic Rydberg molecules studied experimentally or theoretically molecules with such symmetry groups are most typical. We can cite examples of H_3 (D_{3h} symmetry) (Bordas and Helm, 1991, 1992; Dodhy, 1988; Helm, 1986, 1988; Herzberg, 1981, 1987; Ketterle, 1989; King, 1979; Lembo, 1990; Pan, 1988; Stephens, 1995), Na_3 (D_{3h} symmetry) (Broyer, 1986), H_2O (C_{2v} symmetry) (Petfalakis, 1995), H_2F (C_{2v} symmetry) (Martin, 1996), NH_4 (T_d symmetry) (Herzberg, 1981, 1987; Herzberg and Hougen, 1983; Watson, 1984). At the same time many other molecules are potentially interesting from the point of view of their excited Rydberg states or even Rydberg character of the ground state (Basov and Pavlichenkov, 1996; Boldyrev and Simons, 1992a, 1992b; Chiu, 1986; Mayer and Grant, 1995; Wang, 1994; Weber, 1996; Wright, 1994). Their symmetry groups vary from very simple C_s for HCO (Mayer and Grant, 1995) till the highest icosahedral symmetry I_h for C_{60} (Weber, 1996). That is why we give in this appendix orbits and strata for all possible finite symmetry groups. The list of critical orbits for each symmetry group enable us to give the description of simplest Morse type functions (see Tables XX and XXI in Section IV C).

The Tables listed in this appendix show in column 1 the stabilizer of the stratum. In column 2 closed and generic strata are indicated. We remark once more that some strata are neither closed nor generic. In column 3 the dimension of the stratum is given. For the finite group action on Σ the dimension of the generic stratum is always 4. Column 4 gives the number of orbits in the stratum. If the dimension of the stratum is zero the number of orbits in the stratum is finite. If the dimension of the stratum is positive the number of orbits in the stratum is infinite. We mark it ∞^n with n equal the dimension of the stratum. Column 5 shows the number of points in each orbit. For finite group actions on Σ this number is always finite. Along with Tables of strata and orbits given in this Appendix we give below strata equations for critical strata for some point groups. The

TABLE XXIX. Strata and orbits in the action of C_s s on Σ .

Stabilizer	gc	dim.	number	nature
C_s	c	2	∞^2	1
1	g	4	∞^4	2

TABLE XXX. Strata and orbits in the action of C_{nh} on Σ .

Stabilizer	gc	dim.	number	nature
C_{nh}	c	0	2	1
C_n	c	0	1	2
C_s		2	∞^2	n
1	g	4	∞^4	$2n$

form of equation defining strata depends on the choice of variables (representation).¹⁷ Throughout this paper we use either $x + y$ or $j + k$ representation of the Σ manifold.

For the C_n group action on Σ there is one closed zero dimensional stratum with the stabilizer C_n . Equations defining this stratum in x, y representation are

$$x_3^2 = \frac{1}{2}, \quad y_3^2 = \frac{1}{2}. \quad (C1)$$

In the j, k representation the same equations (C1) are

$$j_3^2 = 1, \quad k_3^2 = 1. \quad (C2)$$

For the C_s group action on Σ the only closed stratum with the stabilizer C_s has dimension two. In x, y and j, k representations the same stratum is given respectively by three equations (C3a) and (C3b):

$$x_1 = -y_1, \quad x_2 = -y_2, \quad x_3 = -y_3, \quad (C3a)$$

$$j_1 = j_2 = 0, \quad k_3 = 0. \quad (C3b)$$

C_{nh} group action on Σ produces two closed strata. The C_{nh} stratum is defined in $x, y, (j, k)$ representation by (C4a) (C4b) respectively)

$$x_3 = y_3 = \pm \frac{1}{2}, \quad (C4a)$$

$$j_3^2 = 1. \quad (C4b)$$

The C_n stratum is defined in $x, y, (j, k)$ representation by (C5a) (C5b) respectively)

$$x_3 = -y_3 = \pm \frac{1}{2}, \quad (C5a)$$

$$k_3^2 = 1. \quad (C5b)$$

¹⁷Remark, that information concerning strata and orbits which listed in Tables in this Appendix does not depend on the representation.

TABLE XXXI. Strata and orbits in the action of S_2 on Σ .

Stabilizer	gc	dim.	number	nature
S_2	c	2	∞^2	1
1	g	4	∞^4	2

TABLE XXXII. Strata and orbits in the action of S_{2n} on Σ .

Stabilizer	gc	dim.	number	nature
S_{2n}	c	0	2	1
C_n	c	0	1	2
S_2		2	∞^2	n
1	g	4	∞^4	$2n$

For the S_2 group action on Σ the S_2 closed stratum is given by the following equations in x, y (C6a) and j, k (C5b) representations.

$$x_1 = y_1, \quad x_2 = y_2, \quad x_3 = y_3, \quad (C6a)$$

$$k^2 = 0. \quad (C6b)$$

APPENDIX D: QUALITATIVE DESCRIPTION OF EFFECTIVE HAMILTONIANS. ANALYSIS BASED ON EQUIVARIANT MORSE-BOTT THEORY

1. Compilation of Bott and Kirwan about the construction of equivariant homology.

We follow in this section the equivariant method developed mainly by Bott (1982), Atiyah and Bott (1982) and Kirwan (1984, 1988). The initial point for the construction of the equivariant theory is a simple remark that if the group action would free all problems disappear. Now the idea is to extend the group action to larger space where its action is free and make necessary calculations on this larger space.

First observation. If U is any space on which G acts freely, then the diagonal action of G on $W \times U$ is free. So, to transform our problem into another one with the free group action we should find a space U in which G acts freely and whose homotopy is trivial (i.e. U is contractible).

TABLE XXXIII. Strata and orbits in the action of C_{nv} (n even) on Σ .

Stabilizer	gc	dim.	number	nature
C_{nv}	c	0	2	1
C_n	c	0	1	2
C_s^v		2	∞^2	n
C_s^d		2	∞^2	n
1	g	4	∞^4	$2n$

TABLE XXXIV. Strata and orbits in the action of C_{nv} (n odd) on Σ .

Stabilizer	gc	dim.	number	nature
C_{nv}	c	0	2	1
C_n	c	0	1	2
C_s		2	∞^2	n
1	g	4	∞^4	$2n$

TABLE XXXV. Strata and orbits in the action of D_n ($n \geq 2$, even) on Σ .

Stabilizer	gc	dim.	number	nature
C_n	c	0	2	2
C_2	c	0	2	n
C_2'	c	0	2	n
1	g	4	∞^4	$2n$

TABLE XXXVI. Strata and orbits in the action of D_n ($n \geq 3$, odd) on Σ .

Stabilizer	gc	dim.	number	nature
C_n	c	0	2	2
C_2	c	0	4	n
1	g	4	∞^4	$2n$

TABLE XXXVII. Strata and orbits in the action of D_{nh} ($n \geq 3$, odd) on Σ .

Stabilizer	gc	dim.	number	nature
C_{nh}	c	0	1	2
C_{nv}	c	0	1	2
C_{2v}	c	0	2	n
C_2	c	0	1	$2n$
C_{1h}		2	∞^2	$2n$
C_s		2	∞^2	$2n$
1	g	4	∞^4	$4n$

TABLE XXXVIII. Strata and orbits in the action of D_{nh} ($n \geq 2$, even) on Σ .

Stabilizer	gc	dim.	number	nature
C_{nh}	c	0	1	2
C_{nv}	c	0	1	2
C_{2v}	c	0	1	n
C_{2v}	c	0	1	n
C_{2h}	c	0	1	n
C_{2v}	c	0	1	n
C_{1h}		2	∞^2	$2n$
C_s		2	∞^2	$2n$
C_s'		2	∞^2	$2n$
1	g	4	∞^4	$4n$

TABLE XXXIX. Strata and orbits in the action of D_{nd} ($n \geq 2$, even) on Σ .

Stabilizer	gc	dim.	number	nature
S_{2n}	c	0	1	2
C_{nv}	c	0	1	2
C_{2v}	c	0	1	n
C_{2v}	c	0	1	n
C_{2h}	c	0	1	n
C_{2v}	c	0	1	n
C_{1h}		2	∞^2	$2n$
C_s		2	∞^2	$2n$
C'_s		2	∞^2	$2n$
1	g	4	∞^4	$4n$

TABLE XLIV. Strata and orbits in the action of O_h on Σ .

Stabilizer	gc	dim.	number	nature
C_{4v}	c	0	1	6
C_{4h}	c	0	1	6
C_{3v}	c	0	1	8
C_{3h}	c	0	1	8
C_{2v}	c	0	1	12
C_{2h}	c	0	1	12
C_s		2	∞^2	24
C_s^d		2	∞^2	24
1	g	4	∞^4	48

TABLE XL. Strata and orbits in the action of D_{nd} ($n \geq 3$, odd) on Σ .

Stabilizer	gc	dim.	number	nature
S_{2n}	c	0	1	2
C_{nv}	c	0	1	2
C_{2h}	c	0	2	n
C_2	c	0	1	$2n$
C_{1h}		2	∞^2	$2n$
C_s		2	∞^2	$2n$
1	g	4	∞^4	$4n$

TABLE XLV. Strata and orbits in the action of I on Σ .

Stabilizer	gc	dim.	number	nature
C_5	c	0	2	12
C_3	c	0	2	20
C_2	c	0	2	30
1	g	4	∞^4	60

TABLE XLI. Strata and orbits in the action of T on Σ .

Stabilizer	gc	dim.	number	nature
C_3	c	0	4	4
C_2	c	0	2	6
1	g	4	∞^4	12

TABLE XLII. Strata and orbits in the action of T_h on Σ .

Stabilizer	gc	dim.	number	nature
C_{3h}	c	0	2	4
C_3	c	0	1	8
C_{2h}	c	0	1	6
C_{2v}	c	0	1	6
C_s^h		2	∞^2	12
C_s^v		2	∞^2	12
1	g	4	∞^4	24

TABLE XLIII. Strata and orbits in the action of O on Σ .

Stabilizer	gc	dim.	number	nature
C_4	c	0	2	6
C_3	c	0	2	8
C_2	c	0	2	12
1	g	4	∞^4	24

TABLE XLVI. Strata and orbits in the action of I_h on Σ .

Stabilizer	gc	dim.	number	nature
C_{5v}	c	0	1	12
C_{5h}	c	0	1	12
C_{3v}	c	0	1	20
C_{3h}	c	0	1	20
C_{2v}	c	0	1	30
C_{2h}	c	0	1	30
C_s		2	∞^2	60
1	g	4	∞^4	120

It is known that such spaces turned out to exist, be essentially unique, and play an absolutely essential role in all modern topology. Bott gives examples. For $G = U(1) = S_1$, U is a unit sphere in a complex infinite-dimensional Hilbert space. For $G = U(2)$ the corresponding U space is the space of 2-frames in a complex infinite-dimensional Hilbert space.

As soon as U is known for a given G , the homotopy quotient W_G of any action is defined by

$$W_G = (U \times W)/G, \quad (D1)$$

assuming that G acts diagonally on the product.

The construction of W_G enables one to introduce the equivariant version, F^G , of any functor F by imposing

$$F^G(W) = F(W_G) \quad (D2)$$

This means that the equivariant functor on the initial space W is defined through the ordinary functor on the quotient space W_G .

5. The space U/G plays the role of the homotopy quotient of the trivial action of G on a point. This space is usually denoted as BG and is referred to as the classifying space of G . It is a topological space which somehow reflects both the algebraic and the topological properties of G .

In the equivariant Morse series a non-degenerate critical point contributes the expression

$$P_{point}^G(t) = P_{BG}(t). \quad (D3)$$

Here $P_{BG}(t)$ is the ordinary Poincaré polynomial for BG , the classifying space of G .

If N is a non-degenerate critical manifold consisting of a single orbit $N = G/H$ then this critical submanifold contributes the expression

$$P_{G/H}^G(t) = P_{BH}(t). \quad (D4)$$

In particular, if the group G acts freely on the critical orbit N , this orbit counts in terms of its index and the ordinary Poincaré polynomial of N/G which in this case is a *point*.

The classifying spaces and their *ordinary homology* play an essential role in the equivariant theory. Concrete example. For $G = U(1)$, the classifying space $U/G = BG$ is a CP_∞ space. Its Poincaré polynomial has the form

$$P_{CP_\infty}(t) = 1 + t^2 + t^4 + t^6 + \dots = \frac{1}{(1-t^2)} \quad (D5)$$

Trivial example. Let consider the action of the circle S_1 on the two sphere S_2 given by rotation about the z -axis in $\mathbf{R}^3$,

$$S_2: x^2 + y^2 + z^2 = 1. \quad (D6)$$

Let write first Morse counting function and Morse inequalities using ordinary homology for three simple functions z , z^2 , $-z^2$.

$$\mathcal{M}_{f=z}(t) = 1 + t^2, \quad (D7a)$$

$$\mathcal{M}_{f=z^2}(t) = (1+t) + 2t^2, \quad (D7b)$$

$$\mathcal{M}_{f=-z^2}(t) = t(1+t) + 2, \quad (D7c)$$

As soon as the Poincaré polynomial for the S_2 is $(1+t^2)$ it is clear that all three functions satisfies Morse inequalities

$$\mathcal{M}_{f=z}(t) - (1+t^2) = 0, \quad (D8a)$$

$$\mathcal{M}_{f=z^2}(t) - (1+t^2) = (1+t)t, \quad (D8b)$$

$$\mathcal{M}_{f=-z^2}(t) - (1+t^2) = (1+t). \quad (D8c)$$

The function z is perfect in ordinary sense whereas two others are obviously not perfect.

Equivariant calculations for z and z^2 are given by Bott and Kirwan. The equivariant polynomial for the S_2 is

$$P_t^G(S_2) = \frac{1+t^2}{1-t^2}, \quad G = S_1 \quad (D9)$$

The Morse counting polynomial for the function z

$$\mathcal{M}_{f=z}^G(t) = \frac{1}{1-t^2} + \frac{t^2}{1-t^2}, \quad G = S_1 \quad (D10)$$

includes two contributions from two isolated stationary points. The Morse counting polynomial for the function z^2

$$\mathcal{M}_{f=z^2}^G(t) = 1 + \frac{2t^2}{1-t^2}, \quad G = S_1 \quad (D11)$$

includes one contribution from the stationary one dimensional manifold S_1 corresponding to a circular minimum at $z = 0$ and two contributions from two isolated stationary points which are both maxima. It is easy to see that both functions z , z^2 are perfect in the equivariant sense.

The equivariant Morse counting polynomial for the $(-z^2)$ function includes contributions from two isolated stationary points (two minima) which are

$$\frac{2}{1-t^2} \quad (D12)$$

The contribution from the circular maximum at $z = 0$ should be t and

$$\mathcal{M}_{f=-z^2}^G(t) = t + \frac{2}{1-t^2}, \quad G = S_1 \quad (D13)$$

but in such a case the difference between the Morse counting equivariant polynomial and the Poincaré equivariant polynomial

$$\mathcal{M}_{f=-z^2}^G(t) - P^G(t) = \quad (D14)$$

$$t + \frac{2}{1-t^2} - \frac{1+t^2}{1-t^2} = t + 1$$

This result shows that the $(-z^2)$ function satisfies equivariant Morse inequalities, but it is not perfect.

2. $SO(3)$ continuous subgroup.

To find possible Morse-Bott type functions we use here the equivariant Morse inequalities. Strata and orbits of the $SO(3)$ group action on Σ are listed in Table V. There are two Morse counting polynomials. One for critical orbits (which are S_2 manifolds), and another for generic orbits (PR_3 manifolds with the $SO(3)$ group acting freely on this manifold).

We can write the Morse inequalities on the σ manifold in the form

$$\mathcal{M}^{noncrit}(t) + \frac{(1+t^2)\mathcal{M}^{crit}(t)}{1-t^4} - \frac{1+2t^2+t^4}{1-t^4} \quad (D15)$$

$$= (1+t) Q(t), \quad Q(t) \geq 0.$$

We remind that $Q(t) \geq 0$ in (D15) means that all coefficients of the $Q(t)$ polynomial are not negative. Here the $(1-t^4)^{-1}$ stands for the Poincaré polynomial for the universal classifying space of the $SO(3)$ group

$$P_{B(SO(3))}(t) = \frac{1}{1-t^4} \quad (D16)$$

The $(1+2t^2+t^4)$ is the ordinary Poincaré polynomial for the Σ , and the $(1+t^2)$ the ordinary Poincaré polynomial for the S_2 sphere. The form of two Morse counting polynomials is

$$\mathcal{M}^{noncrit}(t) = n_0 + n_1 t, \quad (D17a)$$

$$\mathcal{M}^{crit}(t) = c_0 + c_1 t + c_2 t^2, \quad (D17b)$$

$$c_i \geq 0, \quad c_0 + c_1 + c_2 = 2. \quad (D17c)$$

In fact it is easy to see that $c_1 = 0$, otherwise the left side of the Morse inequalities is not a finite polynomial. To simplify the analysis we can just look for three different cases corresponding to three different polynomials

$$\mathcal{M}^{crit}(t) = 1 + t^2, \quad (D18a)$$

$$\mathcal{M}^{crit}(t) = 2t^2, \quad (D18b)$$

$$\mathcal{M}^{crit}(t) = 2. \quad (D18c)$$

Three associated Morse inequalities are written in the form

$$n_0 + n_1 t = (1+t) Q(t), \quad (D19a)$$

$$n_0 + 1 + n_1 t = (1+t) Q(t), \quad (D19b)$$

$$n_0 - 1 + n_1 t = (1+t) Q(t). \quad (D19c)$$

So, we have an obvious answer. When two critical orbits are minimum and maximum, the number of generic maxima is equal to the number of generic minima. When both critical orbits are minima, the number of generic maxima is larger by one than the number of generic minima. When both critical orbits are maxima, the number of generic maxima is smaller by one than the number of generic minima.

3. C_∞ continuous subgroup.

There are four isolated one point C_∞ orbits and a generic stratum of C_1 orbits. So any C_∞ invariant function on Σ possesses at least four stationary points coinciding with critical orbits and probably some extra S_1 critical manifolds corresponding to generic C_1 orbits. We give below the complete list of qualitatively different C_∞ invariant functions. This means that we characterize each function by several numbers giving the numbers of critical orbit of each Morse index over each stratum. As soon as for this concrete example four C_∞ orbits are critical and they should have even Morse index there are 15 possible class of functions which may be differed by their behavior on the C_∞ stratum. Within each such class further classification of generic functions should take into account the number of S_1 critical manifolds of each Morse index.

We will use Morse counting polynomials separately for C_∞ and C_1 strata. For the C_∞ stratum this polynomial has the form

$$\mathcal{M}^{C_\infty}(t) = n_0 + n_2 t^2 + n_4 t^4, \quad (D20a)$$

$$n_0 + n_2 + n_4 = 4, \quad n_i \geq 0. \quad (D20b)$$

It simply indicates that there are n_0 C_∞ orbits with Morse index 0, n_2 C_∞ orbits with Morse index 2, and n_4 C_∞ orbits with Morse index 4. It may be verified that there are 15 different possibilities to choose n_0, n_2, n_4 to be integers and nonnegative and to satisfy $n_0 + n_2 + n_4 = 4$.

Similar counting polynomial for critical C_1 orbits is a polynomial of the third degree

$$\mathcal{M}^{C_1}(t) = k_0 + k_1 t + k_2 t^2 + k_3 t^3, \quad (D21)$$

because any C_1 orbit is a S_1 manifold. It is clear that k_i should be integers and nonnegative but further restrictions on k_i should follow from the Morse theory.

If we apply the approach based on ordinary homology the Morse inequalities take the form

$$\mathcal{M}^{C_1}(t) (1+t) + \mathcal{M}^{C_\infty}(t) - (1+2t^2+t^4) \quad (D22)$$

$$= (1+t)Q(t), \quad Q(t) \geq 0.$$

Unfortunately this form of Morse inequalities is insufficient in several cases. For example, it gives no restrictions on the number and type of C_1 stationary orbits for the class of C_∞ invariant functions characterized by

$$\mathcal{M}^{C_\infty}(t) = 1 + 2t^2 + t^4 \quad (D23)$$

Better results can be obtained from using the equivariant version of Morse inequalities. In such a case contributions from C_∞ and C_1 stationary orbits count differently and the equivariant Morse inequalities take the form

$$\mathcal{M}^{C_1}(t) + \frac{\mathcal{M}^{C_\infty}(t)}{1-t^2} - \frac{1+2t^2+t^4}{1-t^2} = (1+t)Q(t), \quad (D24a)$$

$$Q(t) \geq 0. \quad (D24b)$$

TABLE XLVIII. Classification of qualitatively different C_∞ invariant Hamiltonians by their complexity.

Level of complexity	Numbers of qualitatively different C_∞ invariant Hamiltonians
0	1
1	4
2	9
3	14
4	26
5	24
6	52
7	42

Now we can even forget our previous statement about existence of 15 classes of functions with respect to their behavior on C_∞ stratum. These 15 classes may be re-discovered from the equivariant Morse inequalities. The simple requirement is that the left side of the last equation should be a polynomial. Further step is to find restrictions on $\mathcal{M}^{C_1}(t)$ for each of 15 different classes of functions. These restrictions follow from the fact that the left part should be a polynomial of degree three and it should be divisible by $(1+t)$. So, the $\mathcal{M}^{C_1}(t)$ being the polynomial of degree three should depend for each class on three integer numbers.

We summarize results in the Table XLVII.

There is only one type of simplest C_∞ invariant Hamiltonian. It is characterized by the absence of critical manifolds of nonzero dimension. The next level of complexity includes Hamiltonians with one critical manifold on the C_1 stratum. There are four such Hamiltonians which belong to different classes with respect to their behavior on the C_∞ stratum. To give the list of qualitatively different Hamiltonians of the next level of complexity (those possessing two C_1 stationary orbits) it should be noted that within each class all Hamiltonians have the same parity of the number of C_1 stationary orbits. This is due to the fact that increasing any of a, b, c coefficient by one results in the increase of the number of stationary C_1 orbits by two. So, the set of Hamiltonians of the second level of complexity includes three qualitatively different Hamiltonians from the class $1 + 2t^2 + t^4$ and six another Hamiltonians (each from different class). The number of qualitatively different Hamiltonians increase rapidly with the increase of complexity. (See Table XLVIII showing numbers of qualitatively different Hamiltonians for several low level of complexity.)

It is interesting to note that among qualitatively different function constructed above there are 7 which are perfect in the equivariant sense (i.e $Q(t)$ is identically zero in the equivariant Morse inequalities). All these perfect in the equivariant sense functions belong to different classes with respect to their behavior on the C_∞ stratum. It is evident that they are the most simple functions within their class but they can have several C_1 critical orbits. There is one perfect function with 0-level of complexity

(it belongs to class $(1 + 2t^2 + t^4)$), two perfect functions characterized by the 1-st level of complexity (they are from classes $(3t^2 + t^4)$ and $(1 + t^2 + 2t^4)$ correspondingly), two perfect functions characterized by the 2-nd level of complexity (from classes $(2t^2 + 2t^4)$ and $(1 + 3t^4)$), one perfect function with the third level of complexity (class $(t^2 + 3t^4)$), and one perfect function with the 4-th level of complexity (class $(4t^4)$).

APPENDIX E: PHYSICAL EXAMPLES OF SYSTEMS AND PHENOMENA WITH CONTINUOUS SUBGROUPS OF $O(3) \wedge T$ AS SYMMETRY GROUPS

We have studied in the main text the group $O(3) \wedge T$ and its subgroups. There are four proper three dimensional subgroups and 16 one dimensional subgroups. Only some of them are studied in the paper, namely those which are tightly related with the proposed physical examples. In this appendix we give the realisation of all different subgroups as symmetry group of some physical systems. This appendix may be considered as extension of the famous paper by P. Curie (1894) which concerns the symmetry of physical phenomena and gives the realization of five continuous one dimensional symmetry groups as symmetry groups of different physical phenomena. We give below more detailed description of symmetry effects taking into account the time reversal.

1. One dimensional Lie subgroups of $O(3) \wedge T$

We start with one dimensional groups. Let us consider a homogenous fixed cylinder as initial classical object. His symmetry group is the $D_{\infty h} \wedge T$ group which is the maximal one dimensional subgroup of $O(3) \wedge T$. Further we introduce several elementary excitations (physical perturbations) which correspond to different broken symmetry. In Table XLIX we indicate all symmetry elements with respect to which the perturbation introduced is invariant.

They correspond exactly to the seven one dimensional symmetry groups with four connected components listed in Table VIII. We explain them shortly below.

i) Homogenous dilation or compression of the system. This perturbation breaks time reversal invariance. The associated symmetry group is $D_{\infty h}$.

ii) Axis asymmetry can be introduced by static form asymmetry (transformation of cylinder into pear form object) or by constant electric field parallel to the symmetry axis. The corresponding symmetry group is $C_{\infty v} \wedge T$.

iii) Double twist is the static perturbation of the cylinder such that the middle section of the cylinder is twisted in one direction whereas two ends are twisted in the same opposite direction. The corresponding symmetry group is $C_{\infty h} \wedge T$.

TABLE XLVII. Classification of qualitatively different C_∞ invariant Hamiltonians.

$\mathcal{M}^{C_\infty}(t)$	$\mathcal{M}^{C_1}(t)$	Coefficients	Simplest $\mathcal{M}^{C_1}(t)$
$1 + 2t^2 + t^4$	$a + (a+b)t + (b+c)t^2 + ct^3$	$a, b, c \geq 0$	0
$3t^2 + t^4$	$(a+1) + (a+b)t + (b+c)t^2 + ct^3$	$a, b, c \geq 0$	1
$2 + t^2 + t^4$	$a + (a+1+b)t + (b+c)t^2 + ct^3$	$a, b, c \geq 0$	t
$1 + t^2 + 2t^4$	$a + (a+b)t + (b+c+1)t^2 + ct^3$	$a, b, c \geq 0$	t^2
$1 + 3t^2$	$a + (a+b)t + (b+c)t^2 + (c+1)t^3$	$a, b, c \geq 0$	t^3
$3 + t^4$	$a + (a+2+b)t + (b+c)t^2 + ct^3$	$a, b, c \geq 0$	$2t$
$4t^2$	$(a+1) + (a+b)t + (b+c)t^2 + (c+1)t^3$	$a, b, c \geq 0$	$1 + t^3$
$2 + 2t^2$	$a + (a+1+b)t + (b+c)t^2 + (c+1)t^3$	$a, b, c \geq 0$	$t + t^3$
$2 + 2t^4$	$a + (a+1+b)t + (b+c+1)t^2 + ct^3$	$a, b, c \geq 0$	$t + t^2$
$2t^2 + 2t^4$	$(a+1) + (a+b)t + (b+c+1)t^2 + ct^3$	$a, b, c \geq 0$	$1 + t^2$
$1 + 3t^4$	$a + (a+b)t + (b+c+2)t^2 + ct^3$	$a, b, c \geq 0$	$2t^2$
$3 + t^2$	$a + (a+b+2)t + (b+c)t^2 + (c+1)t^3$	$a, b, c \geq 0$	$2t + t^3$
$t^2 + 3t^4$	$(a+1) + (a+b)t + (b+c+2)t^2 + ct^3$	$a, b, c \geq 0$	$1 + 2t^2$
4	$a + (a+3+b)t + (b+c)t^2 + (c+1)t^3$	$a, b, c \geq 0$	$3t + t^3$
$4t^4$	$(a+1) + (a+b)t + (b+c+3)t^2 + ct^3$	$a, b, c \geq 0$	$1 + 3t^2$

iv) Uniform twist is just a simple static twist of two opposite ends of the cylindre in opposite directions. The symmetry group is $D_\infty \wedge T$. Much simple physical realization of the same symmetry group can be reached with cylinder filled by isotrope optically active liquid.

v) Axial current can be realized for example as an electric or thermic current along the axe of cylindre. This perturbation breaks in particular the time reversal invariance. The symmetry group is $C_{\infty v} \wedge T_h$.

vi) Angular current can be realised as uniform rotation of the cylindre, or as constant magnetic field parallel to the axis (solenoid magnetic field). The symmetry group is $C_{\infty h} \wedge T_v$.

vii) Two opposite angular currents can be constructed with two rotations, two electric circular currents or a magnetic field parallel to the axis and varying linearly along the axis and passing through the zero in the equatorial plane of the cylinder. The symmetry group is $D_\infty \wedge T_v$.

Since there are four plus signs in each column of Table XLIX each two component symmetry group can be obtained by three different pairs of perturbations taken from Table XLIX. Following realisation can be proposed for example.

a) Simultaneous application of "angular current" and "axial current" gives the system with $C_\infty \wedge T_2$ symmetry. This formal perturbation can be realised for example by the propagation of a circular polarised light parallel to the cylinder axis.

b) Simultaneous application of "two opposite angular currents" and axial current gives system with $C_{\infty h} \wedge T_h$ symmetry.

c) Uniform twist and axis asymmetry together reduces the symmetry till $C_\infty \wedge T$.

d) Axis asymmetry together with axial current give the symmetry group $C_\infty \wedge T_v$.

e) Axis asymmetry together with axial current give $C_{\infty v}$ symmetry group.

f) Double twist plus angular current leads to $C_{\infty h}$ symmetry group.

g) Twist plus two oppisite angular currents yeild D_∞ symmetry group.

h) To obtain the C_∞ symmetry group we can apply three elementary excitations, for example, static axis asymmetry, axial current, and angular current.

Several groups from the complete list above naturally arise as symmetry groups of simple quantum system.

$C_{\infty v} \wedge T$ is the symmetry group for the atom in static electric field or for rydberg states of heteronuclear diatomic molecule.

$C_{\infty h} \wedge T_v$ is the symmetry group of an atom in constant magnetic field (Zeeman effect).

$C_\infty \wedge T_v$ is the maximal commun subgroup of $C_{\infty v} \wedge T$ and $C_{\infty h} \wedge T_v$. Thus it corresponds to the symmetry of atom under the simultaneous presence of two parallel magnetic and electric fields.

$D_{\infty h} \wedge T$ group is the symmetry group for rydberg states of homonuclear diatomic molecule, or of the quadratic Zeeman effect.

All these examples have been studied in the main body of the paper. Another interesting quantum example is given by circularily polarised photon. It is characterised by the group $C_\infty \wedge T_2$.

2. Three dimensional Lie subgroups of $O(3) \wedge T$

Electric charge has complete $O(3) \wedge T$ symmetry. In physically reasonable approximation ^4He atom in its ground state gives another example of system with $O(3) \wedge T$ symmetry.

Spherically symmetric outgoing wave is the system with $O(3)$ symmetry. We can consider space dilation or compression as an example of perturbation breaking the time reversal symmetry. Such perturbation physically can be realised if atom is supposed to be in the spherical

TABLE XLIX. Description of symmetries of "elementary perturbations" in terms of continuous and discrete symmetry elements. Sign + means that the corresponding element belongs to the symmetry group.

C_∞	C_v	C_h	C_2	T	T_v	T_h	T_2	Perturbations ^a
+	+	+	+					Dilation (compression)
+	+			+	+			Axis asymmetry
+		+		+		+		Double twist
+			+	+			+	Uniform twist
+	+					+	+	Axial current
+		+			+		+	Angular current
+			+		+	+		Two opposite angular currents
+	+	+	+	+	+	+	+	Unperturbed cylinder

^aNote that lines of the table follow the same order as lines in Table VIII

box with varying radius. ^4He atom within the fullerene cage under varying pressure gives approximate physical realization of the effect in the molecular domain.

To realise the $SO(3) \wedge T$ symmetry group as the symmetry group of a physical system we can take "relatively" stable particle which is a pseudo scalar. π meson is an example. $\pi^\pm$ can be considered as stable for time much smaller than $\sim 10^{-8}$ s. Macroscopic example of this symmetry group is given by isotropic optically active liquid.

Magnetic monopole gives an example of a system with the invariance symmetry group $SO(3) \wedge T_s$.

Finally the disintegration of π meson is the process which is invariant with respect to the $SO(3)$ symmetry group only.

REFERENCES

- Abraham, R., and J.R. Marsden, 1978, *Foundations of Mechanics* (Benjamin/Cummings, Don Mills, Ont.).
- Arnol'd, V. I., 1981, *Mathematical Methods of Classical Mechanics* (Springer, New York).
- Arnol'd, V. I., 1988, Ed. *Modern Problems in Mathematics: Dynamical Systems*, Vols. 1-8 (Springer, Berlin, 1988 - 1993).
- Atiyah, M. F., and R. Bott, 1982, "The Yang-Mills equations over Riemann surfaces." *Philos. Trans. R. Soc. (London)* **A 308**, 523-615.
- Avron, J. E., A. Raveh, and B. Zur, 1988, "Adiabatic quantum transport in multiply connected systems," *Rev. Mod. Phys.* **60**, 873-915.
- Avron, J. E., R. Seiler, and B. Simon, 1983, "Homotopy and quantization in condensed matter physics," *Phys. Rev. Lett.* **51**, 51-53.
- Aymar, M., 1984, "Rydberg series of alkaline-earth atoms Ca through Ba. The interplay of laser spectroscopy and multichannel quantum defect analysis," *Phys. Rep.* **110**, 163-200.
- Aymar, M., C. H. Greene, and E. Luc-Koenig, 1996, "Multichannel Rydberg spectroscopy of complex atoms," *Rev. Mod. Phys.* **68**, 1015-1123.
- Bander, M., and C. Itzykson, 1966, "Group theory and the hydrogen atom, I, II," *Rev. Mod. Phys.* **38**, 330-345, 346-358.
- Basov, S. S., and I. M. Pavlichenkov, 1996, "Stabilization of the metastable rotational axis of an asymmetrical rotor by the orbital motion of a particle," *Yad. Fiz.* **59**, 99-109; [*Phys. At. Nucl. (Russia)* **59**, 91-101].
- Beims, M. W., and G. Alber, 1993, "Bifurcations of electronic trajectories and dynamics of electronic Rydberg wave packets," *Phys. Rev. A*, **48**, 3123-3129.
- Bellissard, J., 1989, "Gap labelling theorems for Schrödinger operators," in *From number theory to physics*, M. Waldschmidt, P. Moussa, J.-M. Luck, and C. Itzykson (Eds), Springer, Berlin.
- Biedenharn, L. C., and J.D. Louck, 1981, *Angular momentum in Quantum Physics* (Addison-Wesley).
- Bixon, M., and J. Jortner, 1996, "The electronic quasicontinuum," *J. Phys. Chem.* **100**, 11914-11919.
- Boiteux, M., 1973, "The three-dimensional hydrogen atom as a restricted four-dimensional harmonic oscillator," *Physica* **65**, 381-395.
- Boiteux, M., 1982, "Theory of nonbijective canonical transformations in mechanics: Application to the Coulomb problem," *J. Math. Phys.* **23**, 1311-1314.
- Boldyrev, A. I., and J. Simons, 1992a, "Rydberg bonding in $(\text{NH}_4)_2$," *J. Phys. Chem.* **96**, 8840-8843; Correction **97**, 1470.
- Boldyrev, A. I., and J. Simons, 1992b, "Theoretical search for large Rydberg molecules NH_3CH_3 , $\text{NH}_2(\text{CH}_3)_2$, $\text{NH}(\text{CH}_3)_3$, $\text{N}(\text{CH}_3)_4$," *J. Chem. Phys.* **97**, 6621-6627.
- Bordas, Ch., M. Broyer, J. Chevalerey, P. Labastie, and S. Martin, 1985, "Multichannel quantum defect theory analysis of the Rydberg spectrum of Na_2 ," *J. Phys. (Paris)* **46**, 27-38.
- Bordas, Ch., and H. Helm, 1991, "Predissociation of H_3 near its ionization threshold induced by very weak electric fields," *Phys. Rev. A*, **43**, 3645-3652.
- Bordas, Ch., and H. Helm, 1992, "Stark effect in triatomic hydrogen Rydberg states," *Phys. Rev. A*, **45**, 387-402.
- Bordas, Ch., L. J. Lembo, and H. Helm, 1991, "Spectroscopy and multichannel quantum-defect theory analysis of the np Rydberg series of H_3 ," *Phys. Rev. A*, **44**, 1817-1827.
- Boris, S. D., S. Brandt, H. D. Dahmen, T. Strohm, and M. L. Larsen, 1993, "Quantum mechanical motion of Gaussian wave packets on elliptical and hyperbolic Kepler orbits in the Coulomb field," *Phys. Rev. A*, **48**, 2574-2585.
- Bott, R., 1982, "Lecture on Morse theory, old and new," *Bull. Am. Math. Soc.* **7**, 331-358.
- Braun, P. A., 1993, "Discrete semiclassical methods in the theory of Rydberg atoms in external fields," *Rev. Mod. Phys.* **65**, 115-161.
- Braun, P. A., and E. A. Solov'ev, 1984, "The Stark effect for the hydrogen atom in a magnetic field," *Zh. Eksp. Teor. Fiz.* **86**, 68-83 [*Sov. Phys. JETP* **59**, 38-46].
- Brodersen, S., and B. Zhilinskii, 1995a, "Transfer of clusters between the vibrational components of CF_4 ," *J. Mol. Spectrosc.* **169**, 1-17.

Brodersen, S., and B. Zhilinskii, 1995b, "The rotational structure of the vibrational states and substates of symmetry E in CF_4 ," J. Mol. Spectrosc. **172**, 303-318.

Broyer, M., G. Delacrétaz, P. Labastie, R. L. Whetten, J. P. Wolf, and L. Wöste, 1986, "Spectroscopy of Na_3 ," Z. Phys. D - Atoms, Molecules and Clusters,

Burnside, W., 1911, *Theory of Groups of Finite Order*, Cambridge Univ. Press, reprinted by Dover, New York, 1955.

Byers Brown, W., and E. Steiner, 1966, "On the electronic energy of a one-electron diatomic molecule near the united atom," J. Chem. Phys. **44**, 3934-3940.

Cacciani, P., C. Delsart, E. Luc-Koenig, and J. Pinard, 1992, "Laser spectroscopic studies of the Stark structure of the $n = 35$ hydrogen diamagnetic manifold in parallel fields," J. Phys. B: At. Mol. Opt. Phys. **25**, 1991-2000.

Cacciani, P., S. Liberman, E. Luc-Koenig, J. Pinard, and C. Thomas, 1989, "Anticrossing effects in Rydberg states of lithium in the presence of parallel magnetic and electric fields," Phys. Rev. A, **40**, 3026-3035.

Cacciani, P., E. Luc-Koenig, J. Pinard, C. Thomas, and S. Liberman, 1988, Rydberg atoms in parallel magnetic and electric fields: I. Experimental studies of the odd diamagnetic multiplet of lithium; n mixing and core effects." J. Phys. B: At. Mol. Opt. Phys. **21**, 3473-3498; "II. Theoretical analysis of the Stark structure of the diamagnetic manifold of hydrogen," 3499-3521; "III. Experimental investigations of the Stark structure of the diamagnetic manifold of lithium," 3523-45.

Cavalli, A., G.D'Ariano, and L. Michel, 1985, "Compact manifolds of coherent states invariant by semi simple Lie groups," Ann. Inst. Henri Poincaré, **44**, 173-193.

Chevalley, C., 1955, "Invariants of finite groups generated by reflections," Amer. J. Math., **77**, 778-782.

Child, M. S., and L. Halonen, 1984, "Overtone frequencies and intensities in the local mode picture," Adv. Chem. Phys. **57**, 1.

Chiu, Ying-Nan, 1986, "Crystal-field theory for the Rydberg states of polyatomic molecules," Can. J. Phys. **64**, 782-795.

Clark, W., C. H. Greene, and G. Miecznik, 1996, "Anisotropic interaction potential between a Rydberg electron and an open-shell ion," Phys. Rev. A, **53**, 2248-

2261.

Coulson, C. A., and A. Joseph, 1967, "A constant of the motion for the two-centre Kepler problem," Int. J. Quant. Chem. **1**, 337-347.

Curie, P., 1894, "Sur la symétrie dans les phénomènes physiques, symétrie d'un champ électrique et d'un champ magnétique," J. Phys. (Paris), III, 393-416.

Cushman, R. H., and L. M. Bates, 1997 *Global aspects of classical integrable systems*, Birkhäuser, Basel.

Dabrowski, I., G. DiLorenzo, G. Herzberg, J. W. C. Johns, D. A. Sadovskii, and M. Vervloet, 1992, "Spectra of the rare gas hydrides. IV. Three new bands of argon deuteride involving a low-lying " p " Rydberg state," J. Chem. Phys. **97**, 7093-7110.

Dabrowski, I., and D. A. Sadovskii, 1994, "Spectra of the rare gas hydrides. V. the np Rydberg series of KrD ," Mol. Phys. **81**, 291-326.

Davies, P. B., M. A. Guest, and R. J. Stickland, 1990, "Infrared laser spectroscopy of H_2 and D_2 Rydberg states. I. Application of the polarization model," J. Chem. Phys., **93**, 5408-5416.

Delande, D., and J. C. Gay, 1986, "The hydrogen atom in a magnetic field. Spectrum from the Coulomb dynamical group approach," J. Phys. B: At. Mol. Phys. **19**, L173-L178.

Delande, D., and J. C. Gay, 1988, "A new method for producing circular Rydberg states," Europhys. Lett. **5**, 303-308.

Delande, D., and J. C. Gay, 1991, "Supersymmetric factorization for Rydberg atoms in parallel electric and magnetic fields," Phys. Rev. Lett. **66**, 3237-3240.

Delande, D., K. T. Taylor, M. H. Halley, T. van der Veldt, W. Vassen, and W. Hogervorst, 1994, "Scaled energy spectra of non-hydrogenic Rydberg atoms in a magnetic field," J. Phys. B: At. Mol. Opt. Phys. **27**, 2771-2784.

Delos, J. B., S.K. Knudson, and D.W. Noid, 1983, "Highly excited states of a hydrogen atom in a strong magnetic field," Phys. Rev. A **28**, 7-21.

Dietrich, H.-J., K. Müller-Dethlefs, and L. Ya. Baranov, 1996, "Fractional Stark state selective electric field ionization of very high- n Rydberg states of molecules," Phys. Rev. Lett. **76**, 3530-3533.

- Dodhy, A., W. Ketterle, H.-P. Messmer, and H. Walther, 1988, "A zero Kelvin Rydberg spectrum of H_3 ," *Chem. Phys. Lett.* **151**, 133-137.
- Dorney, A., J., and J.K.G. Watson, 1972, "Forbidden rotational spectra of polyatomic molecules. Stark effect and $\Delta J = 0$ transitions of T_d molecules," *J. Mol. Spectrosc.* **42**, 135-148.
- Dubrovin, B. A., S.P. Novikov, and A.T. Fomenko, 1990, *Modern Geometry: Methods and Applications. Part III. Introduction to Homology Theory*, (Springer, New York).
- Duistermaat, J. J. 1980, "On global action-angle coordinates," *Commun. Pure Appl. Math.* **33**, 687-706.
- Dunn, M., T. C. Germann, D. Z. Goodson, C. A., Traynor, J. D. Morgan III, D. K. Watson, and D. R. Herschbach, 1994, "A linear algebraic method for exact computation of the coefficients of the $1/D$ expansion of the Schrödinger equation," *J. Chem. Phys.* **101**, 5987-6004.
- Duval, P, 1964, *Homographies, Quaternions and Rotations*, (Oxford University, Oxford, 1964).
- Englefield, M. J., 1972, *Group Theory and the Coulomb Problem*, (Wiley, New York).
- Fabre, C., P. Goy, and S. Haroche, 1977, "Millimetre resonance in Na Rydberg levels detected by field ionization quantum defects and Stark effect studies," *J. Phys. B. At. Mol. Phys.* **10**, L183-L189.
- Fabre, C., Y. Kaluzny, R. Calabrese, L. Jun, P. Goy, and S. Haroche, 1984, "Study of non-hydrogenic near degeneracies between m sublevels in the linear Stark effect of sodium Rydberg states," *J. Phys. B. At. Mol. Phys.* **17**, 3217-3228.
- Fano, U., and E.Y. Sidky, 1992, "Semianalytic theory of Rydberg electron diamagnetism," *Phys. Rev.* **45**, 4776-4791.
- Farrelly, D., 1994, "Motional Stark effect on Rydberg states in crossed electric and magnetic fields," *Phys. Lett. A* **191**, 265-274.
- Farrelly, D., and K. Krantzman, 1991, "Dynamic symmetry of the quadratic Zeeman effect in hydrogen: Semi-classical quantization," *Phys. Rev. A* **43**, 1666-1668.
- Farrelly, D., and J. A. Milligan, 1992, "Action-angle variables for the diamagnetic Kepler problem," *Phys. Rev. A* **45**, 8277-8279.
- Farrelly, D., T. Uzer, P. E. Raines, J. P. Skelton, and J. Milligan, 1992, "Electronic structure of Rydberg atoms in parallel electric and magnetic fields," *Phys. Rev. A* **45**, 4738-4751.
- Flöthmann, E., J. Main, and K. H. Welge, 1994, "The Kepler ellipses of the hydrogen atom in crossed electric and magnetic fields," *J. Phys. B: At. Mol. Opt. Phys.* **27**, 2821-2833.
- Fock, V., 1936, "Zur Theorie des Wasserstoffatoms," *Z. Physik* **98**, 145.
- Fomenko, A. T., 1983, *Differential geometry and topology. Additional chapters*, (Moscow State University press, Moscow).
- Fox, K., H.W. Galbraith, B.J. Krohn and J.D. Louck, 1977, "Theory of level splitting: spectrum of the octahedrally invariant fourth rank tensor operator," *Phys. Rev.* **15**, 1363-1381.
- Frey, M. T., F. B. Dunning, C. O. Reinhold, and J. Burgdorfer, 1996, "Ionization of very-high- n Rydberg atoms by half-cycle pulses in the short pulse regime," *Phys. Rev. A* **53**, R2929-R2932.
- Friedrich, H., and D. Wintgen, 1989, "The hydrogen atom in a uniform magnetic field - an example of chaos," *Phys. Rep.* **183**, 37-79.
- Fujii, A., and N. Morita, 1994, "Laser spectroscopic investigation of high Rydberg states of NO: decay dynamics near the first ionization threshold," *Laser Chem.* **13**, 259-271.
- Ganesan, K., and K. T. Taylor, 1996, "Rydberg states of the hydrogen atom near a metal surface," *J. Phys. B, At. Mol. Opt. Phys.* **29**, 1293-1306.
- Germann, T. C., D. R. Herschbach, M. Dunn, and D. K. Watson, 1995, "Circular Rydberg states of the hydrogen atom in a magnetic field," *Phys. Rev. Lett.* **74**, 658-661.
- Gilmore, R., 1981, *Catastrophe Theory for Scientists and Engineers* (Wiley, New York).
- Goodson, D. Z., and D. K. Watson, 1993, "Dimensional perturbation theory for excited states of two-electron atoms," *Phys. Rev. A* **48**, 2668-2678.
- Gourlay, M. J., T. Uzer, and D. Farrelly, 1993, "Asymmetric-top description of Rydberg-electron dynamics in crossed external fields," *Phys. Rev. A* **47**,

Greene, C. H., and Ch. Jungen, 1985, "Molecular applications of quantum defect theory," *Adv. At. Mol. Phys.* **21**, 51-121.

Grozdanov, T. P., and E. A. Solov'ev, 1995, "Hidden crossings and the separation constant of a hydrogenlike atom in spheroidal coordinates," *Phys. Rev. A*, **51**, 2630-2633.

Guillemin, V., and S. Sternberg, 1990, *Variations on a theme by Kepler*, Colloquium publications, American Mathematical Society, Vol. 42 (AMS, Providence, RI).

Hamermesh, M., 1964, *Group theory and its application to physical problems*, (Addison-Wesley, Reading).

Harris, N. A., and Ch. Jungen, 1993, "Rydberg states of calcium fluoride," *Phys. Rev. Lett.*, **70**, 2549-2552.

Harter, W. G., and C. W. Patterson, 1977, "Orbital level splitting in octahedral symmetry and SF₆ rotational spectra. I. Qualitative features of high J levels," *J. Chem. Phys.* **66**, 4872-4885.

Harter, W. G., C.W.Patterson, and F.J.Paixao, 1978, "Frame transformation relations and multipole transitions in symmetric polyatomic molecules," *Rev. Mod. Phys.* **50**, 37-56.

Harter, W. G., 1988, "Computer graphical and semiclassical approaches to molecular rotations and vibrations," *Comp. Phys. Rep.* **8**, 319-394.

Hasegawa, H., M.Robnik, and G.Wunner, 1989, "Classical and quantum chaos in the diamagnetic Kepler problem," *Prog. Theor. Phys. Sup.* **98**, 198-286.

Helm, H., 1986, Observation of high- n Rydberg series ($7 < n < 40$) of the H₃ molecule," *Phys. Rev. Lett.* **56**, 42-45.

Helm, H., 1988, Measurement of the ionization potential of triatomic hydrogen," *Phys. Rev. A*, **38**, 3425-3429.

Herrick, D.R., 1982, "Symmetry of the quadratic Zeeman effect for hydrogen," *Phys. Rev. A* **26**, 323-329.

Herrick, D.R., and O. Sinanoglu, 1975, "Comparison of doubly-excited helium energy levels, iso-electronic series, autoionization lifetimes, and group-theoretical configuration-mixing predictions with large-configuration-interaction calculations and experimental spectra," *Phys. Rev. A* **11**, 97-110.

Herzberg, G., 1981, "Rydberg spectra of triatomic hydrogen and of the ammonium radical," *Discussions Faraday Soc.* **71**, 165 - 173.

Herzberg, G., 1987, "Rydberg molecules," *Ann. Rev. Phys. Chem.* **38**, 27 - 56.

Herzberg G. and J. T. Hougen, 1983, "Spectra of the ammonium radical: The Schuster band of ND₄," *J. Mol. Spectrosc.* **97**, 430 - 440.

Herzberg, G., and Ch. Jungen, 1972, Rydberg series and ionization potential of the H₂ molecule," *J. Mol. Spectrosc.* **41**, 425-486.

Hiskes, J. R., 1996, "Molecular Rydberg states in hydrogen negative ion discharge," *Appl. Phys. Lett.* **69**, 755-757.

Howard, J. E., and T. D. Wilkerson, 1995, "Problem of two fixed centers and a finite dipole: A unified treatment," *Phys. Rev. A*, **52**, 4471-4492.

Hulet, R. G., and D. Kleppner, 1983, "Rydberg atoms in "Circular" states," *Phys. Rev. Lett.* **51**, 1430-1433.

Hulthén, L., 1933, "Über die quantenmechanische Herleitung der Balmerterme," *Z. Physik* **86**, 21.

Huppner, B., J. Main, and G. Wunner, 1996, "Nonhydrogenic Rydberg atoms in a magnetic field: a rigorous semiclassical approach," *Phys. Rev. A* **53**, 744-759.

Iken, M. A., F. Borondo, R. M. Benito, and T. Uzer, 1994, "Periodic-orbit spectroscopy of the hydrogen atom in parallel electric and magnetic fields," *Phys. Rev. A* **49**, 2734-2747.

Iwai, T., 1981a, "On reduction of the four-dimensional harmonic oscillator," *J.Math. Phys.* **22**, 1628-1632;

Iwai, T., 1981b, "On a "conformal" Kepler problem and its reduction," *J.Math. Phys.* **22**, 1633-1639.

Iwai, T., and Y. Uwano, 1986, "The four dimensional Kepler problem reduces to the three-dimensional Kepler problem with a centrifugal potential and Dirac's monopole field. Classical theory," *J. Math. Phys.* **27**, 1523-1529.

Jacobson, P. L., R. D. Labelle, W. G. Sturru, R. F. Ward, Jr., and S. R. Lundeen, 1996, "Optical spectroscopy of high L $n = 10$ Rydberg states of nitrogen," *Phys. Rev. A* **54**, 314-319.

- Jaffé, Ch., and P. Brumer, 1980, "Local and normal modes: A classical perspective," *J. Chem. Phys.* **73**, 5646-5658.
- Jarić, M., L. Michel, and R. T. Sharp, 1984, "Zeros of covariant vector fields for the point groups: invariant formulation," *J. Phys. (Paris)* **45**, 1-27.
- Johnson, B. R., J. O. Hirschfelder, and K. H. Yang, 1983, "Interaction of atoms, molecules, and ions with constant electric and magnetic fields," *Rev. Mod. Phys.* **55**, 109-153.
- Jones, R. R., 1996, "Creating and probing electronic wave packets using half-cycle pulses," *Phys. Rev. Lett.* **76**, 3927-3930.
- Jungen, Ch., 1988, "Quantum defect theory for molecules," in *Fundamental Processes of Atomic Dynamics*, ed. by J. Briggs, H. Kleinpoppen, and H. Lutz (Plenum, New York), p. 79-103.
- Jungen, Ch., I. Dabrowski, G. Herzberg, and D. J. W. Kendall, 1989, "High orbital angular momentum states in molecular hydrogen and molecular deuterium. II," *J. Chem. Phys.* **91**, 3926-3933.
- Jungen, Ch., I. Dabrowski, G. Herzberg, and M. Vervloet, 1990, "High orbital angular momentum states in molecular hydrogen and molecular deuterium. III," *J. Chem. Phys.* **93**, 2289-2298.
- Kalinski, M., and J. H. Eberly, 1996a, "New states of hydrogen in a circularly polarized electromagnetic field," *Phys. Rev. Lett.* **77**, 2420-2423.
- Kalinski, M., and J. H. Eberly, 1996b, "Trojan wave packets. Mathieu theory and generation from circular states," *Phys. Rev. A* **53**, 1715-1724.
- Kazanskii, A. K., and V. N. Ostrovskii, 1989, "Equivalent operators for doubly excited states of the helium atom," *J. Phys. B: At. Mol. Opt. Phys.* **22**, 3829-3836.
- Kazanskii, A. K., and V. N. Ostrovskii, 1990, "Rydberg electron in a multipole field," *Zh. Exp. Teor. Fiz.* **97**, 78-86 [*Sov. Phys. JETP* **70**, 43-47].
- Kelleher, D. E., and E. B. Saloman, 1987, "Rydberg states with anisotropic ion cores: Stark effect," *Phys. Rev. A* **35**, 3327-3338.
- Kellman, M. E., 1995, "Algebraic methods in spectroscopy," *Annu. Rev. Phys. Chem.* **46**, 395-421.
- Ketterle, W., H.-P. Messner and H. Walther, 1989, "The ν_1 vibration of H_3^+ and autoionizing Rydberg states of H_3 ," *Europhys. Lett.* **8**, 333-338.
- Kim, S. H., and E. Mazur, 1995, "Rydberg states of HD ," *Phys. Rev. A*, **52**, 992-1004.
- King, H. F., and K. Morokuma, 1979, "Theory of the Rydberg spectrum of triatomic hydrogen," *J. Chem. Phys.* **71**, 3213-3220.
- Kirschner, S., and J. K. G. Watson, 1973, "Sextic centrifugal distortion of tetrahedral molecules," *J. Mol. Spectrosc.* **47**, 347-350.
- Kirwan, F., 1984, *Cohomology of quotients in symplectic and algebraic geometry*, Princeton, New Jersey. Kirwan, F., 1988, "The topology of reduced phase space of the motion of vortices on a sphere," *Physica D* **30**, 99-123.
- König, A., J. Neukammer, K. Vietzke, M. Kohl, H.-J. Grabka, H. Hieronymus, and H. Rinneberg, 1988, "Transition from magnetic to electric-field $F||B$ dominated spectra of barium at threshold," *Phys. Rev. A* **38**, 547-550.
- Krantzman, K. D., A. Milligan, and D. Farrelly, 1992, "Semiclassical mechanics of the quadratic Zeeman effect," *Phys. Rev. A* **45**, 3093-3103.
- Kuwata, M., A. Harada, and H. Hasegawa, 1990, "Derivation and quantisation of Solov'ev's constant for the diamagnetic Kepler motion," *J. Phys. A: Math. Gen.* **23**, 3227-3244.
- Labastie, P., M. C. Bordas, B. Tribollet, and M. Broyer, 1984, "Stroboscopic effect between electronic and nuclear motion in highly excited molecular Rydberg states," *Phys. Rev. Lett.* **52**, 1681-1684.
- Laughlin, C., 1995, "An asymptotic-potential method for high- l Rydberg levels of calcium," *J. Phys. B*, **19**, 2787-2801.
- Lahaye, C. T. W. and W. Hogervorst, 1989, "Stark manifolds and electric-field-induced avoided level crossings in helium Rydberg states," *Phys. Rev. A*, **39**, 5658-5665.
- Lawton, R. T., and M. S. Child, 1979, "Local mode vibrations of water," *Mol. Phys.* **37**, 1799-1807.
- Leboeuf, P., J. Kurchan, M. Feingold, and D. P. Arovas, 1992, "Topological aspects of quantum chaos," *Chaos* **2**, 125-130.

Lee, E., D. Farrelly, and T. Uzer, 1994, "Core induced stabilization and autoionization of molecular Rydberg states," *Chem. Phys. Lett.* **231**, 241-245.

Lembo, L. J., H. Helm, and D. L. Huestis, 1989, "Measurement of vibrational frequencies of the H_3 molecule using two-step photoionization," *J. Chem. Phys.* **90**, 5299-5308.

Lembo, L. J., Ch. Bordas, and H. Helm, 1990, "*f*-electron Rydberg series of triatomic hydrogen," *Phys. Rev. A*, **44**, 1817-1827.

Liu, W., S. Gu, and B. Li, 1996, "Fine structure in a strong magnetic field: Pashen-Back effect reconsidered in Rydberg atoms," *Phys. Rev. A*, **53**, 3044-3049.

Lombardi, M., P. Labastie, M. C. Bordas, and M. Broyer, 1988, "Molecular Rydberg states: Classical chaos and its correspondence in quantum mechanics," *J. Chem. Phys.* **89**, 3479-3490.

Lombardi M., and T. H. Seligman, 1993, "Universal and nonuniversal statistical properties of levels and intensities for chaotic Rydberg molecules," *Phys. Rev. A*, **47**, 3571-3586.

Lyapunov, A. A., 1892, *General Problem of Movement Stability*, (Kharkov, Moscow) in Russian.

Mao, J.-M., and J. B. Delos, 1992, "Hamiltonian bifurcation theory of closed orbits in the diamagnetic Kepler problem," *Phys. Rev. A* **45**, 1746-1761.

Martin, I., A. C. Lavin, M. Velasco, M. O. Martin, J. Karwowski, and G. H. F. Dierksen, 1996, "Quantum defect orbital study of electronic transitions in Rydberg molecules: ammonium and fluoronium radicals," *Chem. Phys.* **202**, 307-320.

Mayer, E., and E. R. Grant, 1995, "Double resonance spectroscopy of the high Rydberg states of HCO. I. A precise determination of the adiabatic ionization potential," *J. Chem. Phys.* **103**, 10513-10519.

McIntosh, H. V., and A. Cisneros, 1970, "Degeneracy in the presence of a magnetic monopole," *J. Math. Phys.* **11**, 896-916.

Merkt, F., S. R. Mackenzie, and T. P. Softley, 1995, "Rotational autoionization dynamics in high Rydberg states of nitrogen," *J. Chem. Phys.* **103**, 4509-4518.

Merkt, F., H. Xu, R. N. Zare, 1996, "Preparation and characterization of long-lived molecular Rydberg states: application to HD," *J. Chem. Phys.* **104**, 950-961.

Michel, L., 1970, "Application of group theory to quantum physics," *Lecture Notes in Physics*, **6**, 36-144.

Michel, L., 1971, "Points critiques des fonctions invariantes sur une *G*-variété," *C. R. Acad. Sci. Paris*, **272**, 433-436.

Michel, L., 1972, "Non linear group actions; smooth actions of compact Lie groups on manifolds," in *Statistical Mechanics and Field Theory* (Israel University Press, Jerusalem) p. 133-150.

Michel, L., 1977, "Invariants polynomiaux des groupes de symétrie moléculaire et cristallographique," in *Proc. 5th Intern. Colloq. Group Theoretical Methods in Physics*, p. 75-91, (Academic Press).

Michel, L., 1979, "Minima of Higgs-Landau potentials," in *Regards sur la Physique contemporaine* (CNRS, Paris), p. 157-203.

Michel, L., 1980, "Symmetry defects and broken symmetry, configurations. Hidden symmetry," *Rev. Mod. Phys.* **52**, 617-650.

Michel, L., and J. Mozrzymas, 1978, "Application of Morse theory to symmetry breaking in Landau theory of second order phase transitions," *Lect. Notes Phys.* **79**, 247-258.

Michels, H. H., and F. E. Harris, 1963, "Molecular orbital studies of excited states of HeH," *J. Chem. Phys.* **39**, 1464-1469.

Michelot, F., and J. Moret-Bailly, 1975, "Expression algébriques approchées de symboles de couplage et de fonctions de base adaptés à la symétrie cubique," *J. Phys. (Paris)*, **36**, 451-460.

Milczewski, J. von, G. H. F. Dierksen, and T. Uzer, 1994, "Classical dynamics of Rydberg electrons in crossed fields: The structure of phase space and chaos-order alternations," *Int. J. Bifurcations and Chaos*, **4**, 905-920.

Milczewski, J. von, G. H. F. Dierksen, and T. Uzer, 1996, "Computation of the Arnol'd Web for the hydrogen atom in crossed electric and magnetic fields," *Phys. Rev. Lett.* **76**, 2890-2893.

Milligan, J. A., and Farrelly D., 1993, "Atomic analogs of local and normal modes: The hydrogen atom in a generalized van der Waals potential," *Phys. Rev.* **47**, 3137-3150.

Mills, I. M., and A. G. Robiette, 1985, "On the relation-

- ship of normal modes to local modes in molecular vibrations," *Mol. Phys.* **56**, 743-765.
- Molien, T., 1897, "Über die Invarianten der linearen Substitutionsgruppe," *Sitzungber. König. Preuss. Akad. Wiss.* 1152-1156.
- Montgomery, D., and C.T. Yang, 1957, "The existence of a slice," *Ann. Math.* **65**, 108-116.
- Morse, M., 1925, "Relations between the critical points of a real function of n independent variables," *Trans. Am. Math. Soc.* **27**, 345-396.
- Mostow, G.D., 1957a, "Equivariant embedding in euclidean space," *Ann. Math.* **65**, 432-446.
- Mostow, G.D., 1957b, "On a conjecture of Montgomery," *Ann. Math.* **65**, 513-516.
- Nekhoroshev, N., 1972, "Action-angle variables and their generalization," *Trans. Mosc. Math. Soc.* **26**, 181-198.
- Niu, Q., D. J. Thouless, and Y.-S. Wu, 1985, "Quantized Hall conductance as a topological invariant," *Phys. Rev. B*, **31**, 3372-3377.
- Palais R. C., 1960, *The classification of G-spaces*, *Memoirs Amer. Math. Soc.* No 36.
- Palais, R. C., 1970, " C^1 -action of compact Lie groups on compact manifolds are equivalent to C^∞ -actions," *Amer. J. Math.* **92**, 748-760.
- Pan, S. and K. T. Lu, 1988, "Triatomic molecular H_3 frame transformation theory of the l -uncoupling effect," *Phys. Rev. A*, **37**, 299-302.
- Patterson, C. W., and W.G. Harter, 1977, "Orbital level splitting in octahedral symmetry and SF_6 rotational spectra. II. Quantitative features of high J levels," *J. Chem. Phys.* **66**, 4886-4892.
- Pavlichenkov, I. M., and B.I. Zhilinskii, 1988, "Critical phenomena in rotational spectra," *Ann. Phys. (N.Y.)* **184**, 1-32.
- Pavlov-Verevkin, V. B., D. Sadovskii, and B. Zhilinskii, 1988, "On the dynamical meaning of the diabolic points," *Europhys. Lett.* **6**, 573-578.
- Pauli, W., 1926, "Über das Wasserstoffspektrum vom Standpunkt der neuen Quantenmechanik," *Z. Physik* **36**, 336-363.
- Perelomov, A. M., 1986, *Generalized Coherent States and their Applications* (Springer, Berlin).
- Petfalakis, I. D., G. Theodorakopoulos, and M. S. Child, 1995, "*Ab initio* multichannel quantum defects for the 1A_1 Rydberg states of H_2O ," *J. Phys. B, At. Mol. Opt. Phys.* **28**, 5179-5192.
- Poincaré, H., 1879, *Thèses*, (Paris); *Oeuvres*, (Gauthier Villard, Paris, 1951).
- Poston, T., and I. Stewart, 1978, *Catastrophe Theory and Its Applications*, (Pitman, London).
- Rabani, E., and R. D. Levine, 1996, "The dynamics of Rydberg states of molecules in the intermediate regime: the role of vibrations," *J. Chem. Phys.* **109**, 1937-1952.
- Raithel, G., and M. Fauth, 1995, "Observation of high angular momentum states of Rydberg atoms in strong magnetic and weak crossed electric fields," *J. Phys. B. At. Mol. Opt. Phys.* **28**, 1687-1706.
- Raithel, G., M. Fauth, and H. Walther, 1991, "Quasi-Landau resonances in the spectra of rubidium Rydberg atoms in crossed electric and magnetic fields," *Phys. Rev. A*, **44**, 1898-1909.
- Raithel, G., M. Fauth, and H. Walther, 1993, "Atoms in strong crossed electric and magnetic fields: Evidence for states with large electric-dipole moments," *Phys. Rev. A*, **47**, 419-440.
- Raithel, G., H. Held, L. Marmet, and H. Walther, 1993, "Rubidium Rydberg atom in strong static field," *J. Phys. B. At. Mol. Opt. Phys.* **27**, 2849-2866.
- Rau, A. R. P., and L. Zhang, 1990, "Mapping degenerate perturbation in atoms onto an asymmetric rotor," *Phys. Rev. A* **42**, 6342-6353.
- Remacle, F., and R. D. Levine, 1996a, "Intramolecular dynamics in a congested set of states: a reduced description of the quantal long time evolution with application to high Rydberg states," *Chem. Phys. Lett.* **257**, 111-118.
- Remacle, F., and R. D. Levine, 1996b, "Decay of high Rydberg states: a paradigm for the intramolecular dynamics in a congested bound level structure coupled to a continuum," *J. Chem. Phys.* **104**, 1399-1414.
- Rinneberg, H., J. Neukammer, G. G. Jönsson, H. Hiernonymus, A. König, and K. Vietzke, 1985, "High- n Rydberg atoms and external fields," *Phys. Rev. Lett.* **55**, 382-385.

- Robnik, M., and E. Schröder, 1985, "Hydrogen atom in a strong magnetic field: calculation of the energy levels by quantising the normal form of the regularised Kepler Hamiltonian," *J. Phys. A: Math. Gen.* **18**, L853-L859.
- Rothery, N. E., C. H. Storry, and E. A. Hessels, 1995, "Precision radio-frequency measurements of high- L Rydberg states of lithium," *Phys. Rev. A*, **51**, 2919-2925.
- Sadovskii, D. A., and D. Delos, 1996, "Bifurcations of periodic orbits of Hamiltonian systems: Analysis using normal form theory," *Phys. Rev. E*, **54**, 2033-2070.
- Sadovskii, D. A., J. A. Shaw, and D. Delos, 1995, "Organization of sequences of bifurcations of periodic orbits," *Phys. Rev. Lett.* **75**, 2120-2123.
- Sadovskii, D. A., and B. I. Zhilinskii, 1988, "Qualitative analysis of vibration-rotation Hamiltonians for spherical top molecules," *Mol. Phys.* **65**, 109-128.
- Sadovskii, D. A., and B. I. Zhilinskii, 1993a, "Group-theoretical and topological analysis of localized rotation-vibration states," *Phys. Rev. A*, **47**, 2653-2671.
- Sadovskii, D. A., and B. I. Zhilinskii, 1993b, "Qualitative study of a model three-level Hamiltonian with $SU(3)$ dynamical symmetry," *Phys. Rev. A*, **48**, 1035-1044.
- Sadovskii, D. A., and B. I. Zhilinskii, 1997, "Tuning the hydrogen atom in crossed field between the Zeeman and Stark limit," unpublished.
- Sadovskii, D. A., B. I. Zhilinskii, and L. Michel, 1996, "Collapse of the Zeeman structure of the hydrogen atom in an external electric field," *Phys. Rev. A*, **53**, 4064-4067.
- Simon, B., 1983, "Holonomy, the quantum adiabatic theorem, and Berry's phase," *Phys. Rev. Lett.* **51**, 2167-2170.
- Sakurai, J. J., 1964, *Invariance Principles and Elementary Particles*. (Princeton Univ. Press, New Jersey).
- Schwarz, G., 1965, "Smooth functions invariant under the action of a compact Lie group," *Topology* **14**, 63-68.
- Schwarz, M., R. Duchowicz, W. Demtröder, and Ch. Jungen, 1988, "Autoionizing Rydberg states of electronic-rotational interactions," *J. Chem. Phys.* **89**, 5460-5472.
- Seipp, I., K. T. Taylor, and W. Schweizer, 1996, "Atomic resonances in parallel electric and magnetic fields," *J. Phys. B, At. Mol. Opt. Phys.* **29**, 1-13.
- Shubnikov, A. V., 1951, *Symmetry and antisymmetry of finite figures*. AN SSSR, Moscow, (in Russian).
- Shubnikov, A. V., and N. V. Belov, 1964, *Coloured Symmetry*. London, Pergamon Press.
- Sloane, N. J. A., 1977, Error correcting codes and invariant theory: new applications of a nineteenth-century technique." *Amer. Math. Monthly*, **84** 82-107.
- Smale, S., 1970, "Topology and mechanics," *Inv. Math.* **10**, 305-331, **11** 45-64.
- Solov'ev, E. A., 1981, "Approximate integral of motion of H atom in a magnetic field," *Pis'ma Zh. Eksp. Teor. Fiz.* **34**, 278-81 [*JETP Lett.* **34**, 265-268].
- Solov'ev, E. A., 1982, "Hydrogen atom in a weak magnetic field," *Zh. Eksp. Teor. Fiz.* **82**, 1762-1771 [*Sov. Phys. JETP*, **55**, 1017-1021].
- Solov'ev, E. A., 1986, "Modification of molecular Rydberg states by superpromotion of the diabatic term to the continuous spectrum," *Zh. Eksp. Teor. Fiz.* **90**, 1165-1171 [*Sov. Phys. JETP*, **63**, 678-681].
- Stanley, R. P., 1977, "Relative invariants of finite groups generated by pseudo-reflections," *J. Algebra*, **49**, 134-148.
- Stanley, R. P., 1979, "Invariants of finite groups and their applications to combinatorics," *Bull. Am. Math. Soc.* **1**, 475-511.
- Stebbing, R. F., and F. B. Dunning, 1983, Eds., *Rydberg States of Atoms and Molecules*, (Cambridge University Press, Cambridge, England).
- Stephens, J. A., and C. H. Greene, 1995, "Rydberg state dynamics of rotating vibrating H_3 and the Jahn-Teller effect," *J. Chem. Phys.* **102**, 1579-1591.
- Stiefel, E., L., and G. Scheifele, 1971, *Linear and Regular Celestial Mechanics* (Springer, Berlin).
- Sturuss, W. G., E. A. Hessels, P. W. Arcuni, and S. R. Lundeen, 1988, "Laser spectroscopy of ($\nu = 0, R = 1$) $10F$ and ($\nu = 0, R = 1$) $10G$ states of H_2 : A test of polarization model," *Phys. Rev. A* **38**, 135-151.
- Tanner, G., K. T. Hansen, and J. Main, 1996, "The semiclassical resonance spectrum of hydrogen in a constant magnetic field," *Nonlinearity* **9**, 1641-1670.

- Thom, R., 1972, *Stabilité Structurelle et Morphogénèse*, (Benjamin, N.Y.).
- Thoss, M., and W. Domcke, 1995, "A model for the quantum dynamics of Rydberg states of large molecules," *Chem. Phys. Lett.* **245**, 364-370.
- Thurston, W. P., 1969, *The geometry and topology of three-manifolds* (Princeton).
- Uzer, T., 1990, "Zeeman effect as an asymmetric top," *Phys. Rev. A* **42**, 5787-5790.
- van der Veldt, T., W. Vassen, and W. Hogervorst, 1993, "Helium Rydberg states in parallel electric and magnetic fields," *J. Phys. B: At. Mol. Opt. Phys* **26**, 1945-1955.
- Wang, J., and R. J. Boyd, 1994, "Electronic structure and bonding in Rydberg molecules: NH_4 , H_3O , and related molecules," *Can. J. Phys.* **72**, 851-855.
- Watson, J. K. G., 1984, "Assignment of the Schüler band of the ammonium radical to the $3p^2F_2 - 3s^2A_1$ electronic transition," *J. Mol. Spectrosc.* **107**, 124-132.
- Watson, J. K. G., 1994, "Effects of a core electric dipole moment on Rydberg states," *Mol. Phys.* **81**, 277-289.
- Weber, J. M., M. W. Ruf, and H. Hotop, 1996, "Rydberg electron transfer to C_{60} and C_{70} ," *Z. Phys. D. At. Mol. Clusters (Germany)* **37**, 351-357.
- Weyl, H., 1939, *The classical groups, Their invariants and representations*, (Princeton Univ., New Jersey).
- Wigner, E., 1959, *Group Theory and its application to the quantum mechanics of atomic spectra*, (Academic, New York).
- Wright, J. S., 1994, "Theoretical search for the Rydberg dimer of H_3 ," *Can. J. Phys.* **72**, 866-870.
- Zakrzewski, J., K. Dupret, and D. Delande, 1995, "Statistical properties of energy levels of chaotic systems: Wigner or non-Wigner?" *Phys. Rev. Lett.* **74**, 522-525.
- Zhang, W. M., D. H. Feng, and R. Gilmore, (1990) "Coherent states: Theory and some applications," *Rev. Mod. Phys.* **62**, 867-927.
- Zhilinskii, B. I., 1979, "Spectra of tensor operators adapted to nonstandard basis. Qualitative features of clustering," *J. Mol. Spectrosc.* **78**, 203-228.
- Zhilinskii, B. I., 1989a, Qualitative analysis of vibrational polyads: N mode case," *Chem. Phys.* **137**, 1-13.
- Zhilinskii, B. I., 1989b, *Teoriya slozhnykh molekulyarnykh spektrov*, (Moscow University Press), in Russian; English title: *Theory of complex molecular spectra*.
- Zhilinskii, B. I., 1996, "Topological and symmetry features of intramolecular dynamics through high resolution molecular spectroscopy," *Spectrochim. Acta A*, **52**, 881-900.
- Zhilinskii, B. I., and S. Brodersen, 1994, "The symmetry of the vibrational components of CF_4 ," *J. Mol. Spectrosc.* **163**, 326-338.
- Zhilinskii, B. I., S. Brodersen, and M. Madsen, 1993, "The pattern of clusters in isolated vibrational components of CF_4 and the semiclassical model," *J. Mol. Spectrosc.* **160**, 192-216.
- Zimmerman, M., M. G. Littman, M. M. Kash, and D. Kleppner, 1979, "Stark structure of the Rydberg states of alkali-metal atoms," *Phys. Rev. A* **20**, 2251-2275.