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EFFECTIVE HAMILTONIANS FOR VIBRATIONAL POLYADS: INTEGRITY BASES APPROACH

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The concepts of group images and integrity bases are used together to obtain the most general forms of the effective Hamiltonians for vibrational polyads, H_{eff}, arising in the two- and three-dimensional vibrational problems. All the possible images for all point groups are found for these two cases. The generating function method is generalized to include the so called diagonality condition satisfied by H_{eff}, and is applied to facilitate the search of the integrity bases needed to construct the most general form of H_{eff}. The generating functions and the corresponding integrity bases are found for all two-dimensional and some three-dimensional vibrational problems.

1. Introduction

Excited vibrational states of small polyatomic molecules have been studied intensively during the last years both by experimentalists and by theoreticians. The interest to this problem is due to the practical applications (separation of isotopes by laser multiphoton dissociation, chemical analysis of molecules in the laboratory and in space, etc.) and to the fundamental investigations of the qualitative features of the energy level systems in molecules (transition to quantum chaos, critical behaviour of isolated finite-particle systems, etc.).

One of the characteristic features of polyatomic molecules is that they very often possess a group of (quasi)degenerate vibrational modes. In this paper we shall treat the case when the fundamental frequencies of such (quasi)degenerate modes considerably differ from those of the other vibrational modes, and when the effects due to Fermi resonances between (quasi)degenerate modes in question and the other molecular vibrations are negligible. The vibrational spectra of molecules satisfying these two conditions contain well separated groups of (quasi)degenerate levels, called vibrational polyads (VPs), corresponding to different excitations of the studied modes.

There are many well known examples of molecular systems exhibiting such VPs (refs. [1–9], and references therein). Two stretching modes of the H_2O molecule have close frequencies; they may be considered together and independently from the bending mode. In spite of the near 1:2 Fermi resonance between bending and stretching frequencies the H_2O molecule serves as a most typical example to study the VPs formed by two quasidegenerate vibrations and to demonstrate the applicability of the local mode model. Molecules with several equivalent valence bonds (NH_3, CH_4, SF_6, C_6H_6, etc.) possess more complicated VPs formed by three, four, six, etc. (quasi)degenerate vibrations. The VPs also can be formed by a single degenerate vibration (ν_3 of NH_3, ν_4 of CH_4, ν_3 of SF_6, etc.) splitted by an anharmonic interaction. One of the most interesting examples is surely the $\nu_3(F_{1u})$ overtones of SF_6-type molecules responsible for the multiphoton exictation processes [4,10].

Various theoretical approaches have been used to study the VPs [1–8]. In all of them the VPs are described with the help of an effective Hamiltonian, H_{eff}, acting only within one VP. Usually, to construct H_{eff} one introduces some smallness parameter and then uses a particular perturbative treatment. Such a procedure leads to H_{eff} in the form of a series expansion in the smallness parameter truncated at some fixed order.

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The alternative approach to the construction of H_{eff} is based on the use of the integrity bases (IBs) (refs. [11–19], and references therein). The IBs are widely used in nuclear, particle, and solid state physics. This approach is especially suited to the study of nonlinear effects and to the application of nonperturbative methods of analysis. We present here the application of the IBs to the construction of H_{eff}.

Section 2 is devoted to the description of the general scheme. The group theoretical aspects are discussed in section 3, where the important notion of the image of the group in a given representation [17,20–22] is explained and all images possible in any vibrational problem with two and three degrees of freedom are given. Several different approaches to the construction of the complete list of linearly independent operators of a given power are discussed in section 4. Using some simple examples, we introduce in this section the powerful technique of the generating functions [11,14,15,19,21,23–32], which has been known in mathematical invariant theory for about a century but is not yet widely accepted by molecular physicists. In section 5 we give the generating functions needed to construct H_{eff} for VPs arising in the vibrational problems with two and three degrees of freedom for almost all point groups. The important new contribution here is the generalization of the notion of the generating function in order to take into account the additional conditions imposed on H_{eff}. Section 6 presents the IBs for all problems with two degrees of freedom and for three-dimensional vibrational problems in the case of three nondegenerate vibrations of any symmetry and three-fold degenerate ones for O and T_d symmetry groups.

2. General principles of the construction of H_{eff}

We suppose that the molecule in question possesses n (quasi)degenerate vibrations, whose different excitations form VPs weakly coupled to other vibrational states of the molecule. To study the distribution of the energy levels within a VP, we shall construct the most general power expansion for H_{eff}.

Let $a_1, ..., a_n$ and $a_1^+, ..., a_n^+$ be the usual annihilation and creation operators for the corresponding vibrational degrees of freedom. H_{eff} has nonzero matrix elements between vibrational states belonging to the same VP only. Thus, the most general power expansion for H_{eff} has the form

$$H_{\text{eff}} = \sum C_{k_1 \ldots k_n m_1 \ldots m_n} (a_1^+)^{k_1} \ldots (a_n^+)^{k_n} \times a_1^{m_1} \ldots a_n^{m_n}. \quad (1)$$

Only terms with the same total power of creation and annnihilation operators are included in eq. (1),

$$\sum k_j = \sum m_j. \quad (2)$$

Further we shall refer to condition (2) as to a diagonality condition.

In many cases the molecular system possesses a symmetry group G and the $2n$ vibrational operators may be characterized by a representation Γ of this group. Symmetry requirements put additional restrictions on the effective Hamiltonian terms. The terms which are invariant with respect to the symmetry group G are the only ones admissible in the expansion (1).

The phenomenological approach to the constructin of H_{eff} consists in taking into account all the terms satisfying the diagonality condition (2), the symmetry requirements, and the condition of Hermiticity.

Usually, H_{eff} is built by a step-by-step construction of the needed power expansion. This procedure quickly becomes very cumbersome as the power increases. Here we shall use a more general scheme based on the use of the IBs. According to general statements of the invariant theory [15,16,23–27] slightly modified for our purposes, given the group G, one may always find a set of $K+L$ homogeneous invariant polynomial operators $I_1, ..., I_K, I_{K+1}, ..., I_{K+L}$, having the following properties. The first K invariants, named the denominator ones, are algebraically independent. The other L invariants, named the auxiliary or numerator ones, are algebraically dependent on the first K invariants and are chosen in such a way that the most general operator, H_{eff}, invariant under the operations of the group G can be written in the form

$$H_{\text{eff}} = \sum_{m_1, \ldots, m_K} C_{m_1 \ldots m_K} \{I_1^{m_1} \ldots I_K^{m_K}\} + \sum_{j=1}^{L} \sum_{m_1 \ldots m_K} C^j_{m_1 \ldots m_K} \{I_{K+j} I_1^{m_1} \ldots I_K^{m_K}\}, \quad (3)$$

where $\{...\}$ denotes symmetrization with respect to a noncommuting invariant operator. It should be

stressed here that the auxiliary invariants enter the expression (3) only in a linear fashion. The set of $K+L$ invariants satisfying the above conditions is called the integrity basis.

The general structure of the IB (the number of the numerator and denominator invariants and their powers with respect to the elementary vibrational operators) can be deduced from the so called generating function (GF) for invariants. The GF, $g(\lambda)$, frequently called the Molien function [23], is defined as a function possessing the following important property: the coefficient c_Ω in the power expansion of this function,

$$g(\lambda)=\sum_{\Omega} c_\Omega \lambda^\Omega \tag{4}$$

is equal to the number of linearly independent invariant operators having the power Ω with respect to the elementary vibrational operators.

The GF can always be written in the canonical form

$$g(\lambda)=\frac{1+\lambda^{\tau_1}+\ldots+\lambda^{\tau_L}}{(1-\lambda^{\sigma_1})\ldots(1-\lambda^{\sigma_K})}. \tag{5}$$

The canonical form of the GF admits a very useful algebraic interpretation. Each denominator term, $(1-\lambda^{\sigma_j})$, corresponds to one of the algebraically independent invariant operators of degree σ_j with respect to an elementary vibrational operator. Each numerator term, λ^{τ_s}, corresponds to an auxiliary invariant of the power τ_s.

Some care must be taken when applying such interpretation, because the canonical form of the GF is not determined in a unique way. For example, we can multiply (or divide, when it is possible) both the denominator and numerator of the canonical form (5) by the term $(1+\lambda^\sigma)$ and thus obtain another canonical form for the same GF. In other words, there always exists a canonical form of the GF for which the above interpretation is correct, but sometimes it is not clear which of the different canonical forms possesses this property. The only way to verify the proper choice of the canonical form is to build the corresponding IB. It should be noted that the canonical form obtained by multiplying from the one which gives the correct IB also leads to the IB which is, however, not the minimal one.

There are many mathematical books and reviews on the invariant theory, and especially on the GF method and its applications to physical problems (refs. [11–19,23–33], and references therein). We therefore restrict here ourselves with the bibliography only.

3. Symmetry classification

To proceed further, we have to remember an important group theoretical concept, introduced by Michel [17,18,20,21] – the concept of the group image.

From the group theoretical viewpoint, the initial information for the problem considered is the molecular symmetry group G and a set of irreducible representations $\Gamma_1\oplus\ldots\oplus\Gamma_n=\Gamma$ corresponding to the elementary annihilation operators which can always be chosen to be irreducible tensors with respect to the group G. Nevertheless, it is the group image, G*, in the representation $\Gamma\otimes\Gamma^*$ rather than the group G itself that determines the symmetry properties of the H_{eff}. The representation $\Gamma\otimes\Gamma^*$ arises from the fact that, for the problem considered, H_{eff} has to satisfy the diagonality condition (2).

Introduction of the group images significantly reduces the number of different symmetry cases to study. Table 1 shows all different images, G*, which arise in the two-dimensional vibrational problem. This problem is more easily treated when one uses the special bilinear combinations of the vibrational operators J, J_α ($\alpha=x, y, z$), or $J, J_3, J_\pm$, given by

$$J_+=(J_-)^+=a_1^+a_2,\quad J_3=(a_1^+a_1-a_2^+a_2)/2,$$
$$J=(a_1^+a_1+a_2^+a_2)/2,\quad J_x=(J_++J_-)/2,$$
$$J_y=(J_+-J_-)/2\mathrm{i},\quad J_z=J_3. \tag{6}$$

This is the well known Schwinger representation for the angular momentum operators [34]. Since J is always a totally symmetric operator with respect to the symmetry group G, we list in table 1 the symmetry of the operators, J_α, only.

Table 2 gives the possible images, G*, for the three-dimensional vibrational problem.

The image depends on the group G considered as an abstract group rather than on its realization as a transformation group. Thus, in tables 1 and 2 we have listed different abstract groups only. Different realizations of the abstract groups as transformation

Table 1
Group images for the two-dimensional vibrational problem. Here: LCD is the largest common divisor; all the representations designated by Γ are one-dimensional; $q=\min(2m, n-2m)$; $k=\mathrm{LCD}(n, 2m)$; $j=\mathrm{LCD}(n, q)$; $\alpha=\mathrm{u}, \mathrm{g}$

Molecular group G	Symmetry of a_1, a_2 in G	Symmetry of J_α operators in G	Image G* as an abstract group
any finite	$\Gamma\oplus\Gamma$ Γ real	$3A_1$	C_1
any finite	$\Gamma\oplus\Gamma_1$ Γ, Γ_1 real, $\Gamma\neq\Gamma_1$	$A_1\oplus 2\Gamma_2$ $\Gamma_2=\Gamma\otimes\Gamma_1$	C_2
C_n $n\geqslant 3$	$\Gamma_m\oplus\Gamma_m^*$ $0<m<n/2$	$\Gamma_0\oplus\Gamma_{2m}\oplus\Gamma_{2m}^*$	$C_{n/k}$
$C_n\otimes C_2$ $n=2p, p\geqslant 2$	$\Gamma_{m\alpha}\oplus\Gamma_{m\alpha}^*$ $0<m<n/2$	$\Gamma_{0g}\oplus\Gamma_{2mg}\oplus\Gamma_{2mg}^*$	$C_{n/k}$
D_n $n\geqslant 3$	E_m $m\neq n/4$	$A_2\oplus E_q$	$D_{n/j}$
$D_n\otimes C_2$ $n=2p, p\geqslant 2$	$E_{m\alpha}$ $m\neq n/4$	$A_{2g}\oplus E_{qg}$	$D_{n/j}$
D_{4p} $p\geqslant 1$	E_p	$A_2\oplus B_1\oplus B_2$	D_2
$D_{4p}\otimes C_2$ $p\geqslant 1$	$E_{p\alpha}$	$A_{2g}\oplus B_{1g}\oplus B_{2g}$	D_2
T	E	$A\oplus E$	C_3
$T\otimes C_2$	E_α	$A_g\oplus E_g$	C_3
O	E	$A_2\oplus E$	D_3
$O\otimes C_2$	E_α	$A_{2g}\oplus E_g$	D_3

groups of the three-dimensional Euclidean space are given in table 3 [35]. It should be noted that in many cases studied here the representations of the bilinear operators $\{a_k^+ a_j\}$ in the image are uniquely defined by the image itself. So, we shall frequently speak about different images, paying no attention to the representation of the bilinear operators unless it is needed specially.

4. Construction of the complete set of polynomial invariant operators

Here we shall describe two possible ways of constructing of the complete set of independent invariant operators satisfying the diagonality condition from elementary creation and annihilation operators.

(A) We may first build the IBs for invariants and all types of covariants using only annihilation operators, a^Γ, transforming according to the corresponding irreducible or reducible representation Γ of the group G. Without any loss of generality, we may always choose Γ to be real. Given the IBs, we can easily construct all independent invariants and covariants of the power Ω with respect to the annihilation operators. We shall denote the set of the independent operators having the power Ω and symmetry type Γ_α by ${}^{\Omega}U_1^{\Gamma_\alpha},\ldots,{}^{\Omega}U_{m_\alpha(\Omega)}^{\Gamma_\alpha}$. Now, all independent invariant operators having power Ω with respect both to annihilation and creation operators and thus satisfying the diagonality condition are given by

$$[({}^{\Omega}U_k^{\Gamma_\alpha})^+({}^{\Omega}U_j^{\Gamma_\alpha})]^{A_1}+[({}^{\Omega}U_j^{\Gamma_\alpha})^+({}^{\Omega}U_k^{\Gamma_\alpha})]^{A_1},\quad k,j=1,\ldots,m_\alpha(\Omega). \tag{7}$$

The total number of the independent invariant operators of power 2Ω is equal to $\sum_\alpha[m_\alpha(\Omega)]^2$.

(B) The second possible way is based on the use of the bilinear combinations $[(a_k^+)^{\Gamma_\alpha}\otimes a_j^{\Gamma_\beta}]^\Gamma$ as the initial ones [36]. In this case, one should take into account the existence of the algebraic dependences among these operators. These dependences are known for the general case of n vibrational degrees of freedom [37]. They are rather complicated for $n\geqslant 3$. The situation is greatly simplified for two vibrations. In this case, we can use the pseudomomentum operators (6) as the initial bilinear combinations. It is clear that here there are only three algebraically indepen-

Table 2
Group images for the three-dimensional vibrational problem. Here: LCD is the largest common divisor; all the representations designated by Γ are one-dimensional; $q=\min(2m, n-2m)$; $l=\mathrm{LCD}(n, m)$; $k=\mathrm{LCD}(n, m, q)$; $j=\mathrm{LCD}(n, q, p-m)$; $\alpha, \beta=\mathrm{u}, \mathrm{g}$; $\alpha\neq\beta$; $i=1, 2$

Molecular group G	Symmetry of a_k operators in G	Symmetry of bilinear combinations $a_n^+ a_m$ in G	Image G* as an abstract group
any finite	3Γ Γ real	$9A$	C_1
any finite	$2\Gamma_1\oplus\Gamma_2$ Γ_1, Γ_2 real, $\Gamma_1\neq\Gamma_2$	$5A\oplus4\Gamma_3$ $\Gamma_3=\Gamma_1\otimes\Gamma_2$	C_2
any finite	$\Gamma_1\oplus\Gamma_2\oplus\Gamma_3$ $\Gamma_1, \Gamma_2, \Gamma_3$ real, $\Gamma_1\neq\Gamma_2\neq\Gamma_3\neq\Gamma_1$	$3A\oplus2\Gamma_4\oplus2\Gamma_5\oplus2\Gamma_6$ $\Gamma_4=\Gamma_1\otimes\Gamma_2, \Gamma_5=\Gamma_1\otimes\Gamma_3,$ $\Gamma_6=\Gamma_2\otimes\Gamma_3$	D_2
T	F	$A\oplus E\oplus2F$	T
$T\otimes C_2$	F_α	$A_g\oplus E_g\oplus2F_g$	T
O	F_i	$A_1\oplus E\oplus F_1\oplus F_2$	O
$O\otimes C_2$	$F_{i\alpha}$	$A_{1g}\oplus E_g\oplus F_{1g}\oplus F_{2g}$	O
I	F_i	$A\oplus F_i\oplus H$	I
$I\otimes C_2$	$F_{i\alpha}$	$A_g\oplus F_{ig}\oplus H_g$	I
T	$A\oplus E$	$3A\oplus3E$	C_3
$T\otimes C_2$	$A_\alpha\oplus E_\alpha$	$3A_g\oplus3E_g$	C_3
$T\otimes C_2$	$A_\alpha\oplus E_\beta$	$3A_g\oplus2E_u\oplus E_g$	$C_3\otimes C_2$ (C_6)
O	$A_i\oplus E$	$2A_1\oplus A_2\oplus3E$	D_3
$O\otimes C_2$	$A_{i\alpha}\oplus E_\alpha$	$2A_{1g}\oplus A_{2g}\oplus3E_g$	D_3
$O\otimes C_2$	$A_{i\alpha}\oplus E_\beta$	$2A_{1g}\oplus A_{2g}\oplus E_g\oplus2E_u$	$D_3\otimes C_2$ (D_6)
C_n $n\geqslant3$	$\Gamma_0\oplus\Gamma_m\oplus\Gamma_m^*$ $0<m<n/2$	$3\Gamma_0\oplus2\Gamma_m\oplus2\Gamma_m^*\oplus\Gamma_{2m}\oplus\Gamma_{2m}^*$	$C_{n/l}$
$C_n\otimes C_2$ $n=2p, p\geqslant2$	$\Gamma_{0\alpha}\oplus\Gamma_{m\alpha}\oplus\Gamma_{m\alpha}^*$ $0<m<n/2$	$3\Gamma_{0g}\oplus2\Gamma_{mg}\oplus2\Gamma_{mg}^*\oplus\Gamma_{2mg}\oplus\Gamma_{2mg}^*$	$C_{n/l}$
$C_n\otimes C_2$ $n=2p, p\geqslant2$	$\Gamma_{0\alpha}\oplus\Gamma_{m\beta}\oplus\Gamma_{m\beta}^*$ $0<m<n/2$	$3\Gamma_{0g}\oplus2\Gamma_{mu}\oplus2\Gamma_{mu}^*\oplus\Gamma_{2mg}\oplus\Gamma_{2mg}^*$	$C_{n/l}\otimes C_2$, n/l even, $C_{2n/l}$, n/l odd
C_n $n=2p, p\geqslant2$	$\Gamma_p\oplus\Gamma_m\oplus\Gamma_m^*$ $0<m<n/2$	$3\Gamma_0\oplus\Gamma_{2m}\oplus\Gamma_{2m}^*\oplus2\Gamma_{p-m}\oplus2\Gamma_{p-m}^*$	$C_{n/j}$
$C_n\otimes C_2$ $n=2p, p\geqslant2$	$\Gamma_{0\alpha}\oplus\Gamma_{m\alpha}\oplus\Gamma_{m\alpha}^*$ $0<m<n/2$	$3\Gamma_{0g}\oplus\Gamma_{2mg}\oplus\Gamma_{2mg}^*\oplus2\Gamma_{(p-m)g}\oplus2\Gamma_{(p-m)g}^*$	$C_{n/j}$
$C_n\otimes C_2$ $n=2p, p\geqslant2$	$\Gamma_{0\alpha}\oplus\Gamma_{m\beta}\oplus\Gamma_{m\beta}^*$ $0<m<n/2$	$3\Gamma_{0g}\oplus\Gamma_{2mg}\oplus\Gamma_{2mg}^*\oplus2\Gamma_{(p-m)u}\oplus2\Gamma_{(p-m)u}^*$	$C_{n/j}\otimes C_2$, n/j even, $C_{2n/j}$, n/j odd
D_n $n\geqslant3$	$A_i\oplus E_m$ $m\neq n/4$	$2A_1\oplus A_2\oplus2E_m\oplus E_q$	$D_{n/k}$
D_{2p} $p\geqslant2$	$B_i\oplus E_m$ $m\neq p/2$	$2A_1\oplus A_2\oplus2E_{p-m}\oplus E_q$	$D_{2p/j}$
D_{4p} $p\geqslant1$	$\Gamma\oplus E_p$ $\Gamma=A_i, B_i$	$2A_1\oplus A_2\oplus2E_p\oplus B_1\oplus B_2$	D_4
$D_n\otimes C_2$ $n=2p, p\geqslant2$	$A_{i\alpha}\oplus E_{m\alpha}$ $m\neq n/4$	$2A_{1g}\oplus A_{2g}\oplus2E_{mg}\oplus E_{qg}$	$D_{n/k}$
	$A_{i\alpha}\oplus E_{m\beta}$ $m\neq n/4$	$2A_{1g}\oplus A_{2g}\oplus2E_{mu}\oplus E_{qg}$	$D_{n/k}\otimes C_2$, n/k even, $D_{2n/k}$, n/k odd
	$B_{i\alpha}\oplus E_{m\alpha}$ $m\neq n/4$	$2A_{1g}\oplus A_{2g}\oplus2E_{(p-m)g}\oplus E_{qg}$	$D_{n/j}$
	$B_{i\alpha}\oplus E_{m\beta}$ $m\neq n/4$	$2A_{1g}\oplus A_{2g}\oplus2E_{(p-m)u}\oplus E_{qg}$	$D_{n/j}\otimes C_2$, n/j even, $D_{2n/j}$, n/j odd
$D_{4p}\otimes C_2$ $p\geqslant1$	$\Gamma_\alpha\oplus E_{p\alpha}$ $\Gamma=A_i, B_i$	$2A_{1g}\oplus A_{2g}\oplus2E_{pg}\oplus B_{1g}\oplus B_{2g}$	D_4
	$\Gamma_\alpha\oplus E_{p\beta}$ $\Gamma=A_i, B_i$	$2A_{1g}\oplus A_{2g}\oplus2E_{pu}\oplus B_{1g}\oplus B_{2g}$	$D_4\otimes C_2$

Table 3
Relation between abstract groups and transformation groups of the three-dimensional Euclidean space [35]

Abstract group	Point group
C_n	C_n, $S_{n/2}$, $C_{n/2h}$ ($n/2$ odd)
$C_n \otimes C_2$	C_{nh} (n even)
D_n	D_n, C_{nv}, $D_{n/2d}$, $D_{n/2h}$ ($n/2$ odd)
$D_n \otimes C_2$	D_{nh} (n even)
U_4	T
$U_4 \otimes C_2$	T_h
σ_4	T_d, O
$\sigma_4 \otimes C_2$	O_h
U_5	I
$U_5 \otimes C_2$	I_h

dent operators, J_α, the operator J being algebraically dependent on them

$$J^2 = J_x^2 + J_y^2 + J_z^2. \tag{8}$$

The relation (8), named syzygy in the invariant theory, enables one to write the general invariant operator in this case in the form

$$P_0(J_\alpha) + JP_1(J_\alpha), \tag{9}$$

where P_0 and P_1 are general polynomials in algebraically independent operators J_α.

Let us now consider some examples of the two procedures mentioned above.

(A) To illustrate the first of them we shall construct the set of independent operators invariant with respect to the point group O and satisfying the diagonality condition starting from the vibrational operators a^{F_2}. The needed GFs, $g(\Gamma_f, \Gamma_i; \lambda)$, are given in table 4. The meaning of these functions is analogous to that of the GF for invariants: the coefficient before λ^Ω in the series expansion of the function $g(\Gamma_f, \Gamma_i; \lambda)$ shows how many linearly independent covariants of power Ω and symmetry type Γ_f can be constructed from the operators transforming according to the irreducible representation Γ_i of the group G. We shall choose basic invariants and covariants as irreducible tensors adopted to the group chain $SU(3) \supset SO(3) \supset O$. We use the standard notation for the irreducible tensors $V^{\Omega(K,m\Gamma)}$, where Ω is the power of the tensor with respect to the elementary tensors a_k and a_k^+; K is its rank, i.e. the irreducible representation of the SO(3) group; Γ is the irreducible representation of the O group, and m is the internal multiplicity index. Table 5 gives the IBs for invariants and all types of covariants built from the creation (or annihilation) operators. We can use them now to construct the complete set of independent operators of any degree satisfying the diagonality condition. For example we list below the operators of the three lowest degrees.

Bilinear operators:

$$[[V^{1(1,F_2)}] + [V^{1(1,F_2)}]]^{A_1}.$$

Biquadratic operators:

$$[[V^{2(0,A_1)}] + [V^{2(0,A_1)}]]^{A_1},$$

$$[[V^{2(2,E)}] + [V^{2(2,E)}]]^{A_1},$$

$$[[V^{2(2,F_2)}] + [V^{2(2,F_2)}]]^{A_1}.$$

Bicubic operators:

$$[[V^{3(3,A_1)}] + [V^{3(3,A_1)}]]^{A_1},$$

$$[[V^{3(3,F_1)}] + [V^{3(3,F_1)}]]^{A_1},$$

$$[[V^{3(3,F_2)}] + [V^{3(3,F_2)}]]^{A_1},$$

$$[[V^{3(3,F_2)}] + [V^{3(1,F_2)}]]^{A_1},$$

$$[[V^{3(1,F_2)}] + [V^{3(3,F_2)}]]^{A_1},$$

$$[[V^{3(1,F_2)}] + [V^{3(1,F_2)}]]^{A_1}.$$

(B) To illustrate our second procedure we shall consider the two-dimensional vibrational problem. As we have mentioned earlier in this case, one may omit the J invariant and construct the IB for the three-dimensional initial representation formed by operators J_α. The complete solution of this problem may be achieved by the traditional formulae of the invariant

Table 4
Generating functions $g(\Gamma_f, \Gamma_i = F_2; \lambda)$ for group $O(T_d)$. Here: $Z = (1-\lambda^2)(1-\lambda^3)(1-\lambda^4)$

Γ_f	A_1	A_2	E	F_1	F_2
g	$1/Z$	λ^6/Z	$(\lambda^2+\lambda^4)/Z$	$(\lambda^3+\lambda^4+\lambda^5)/Z$	$(\lambda+\lambda^2+\lambda^3)/Z$

Table 5
Integrity bases for invariants and covariants constructed from the irreducible tensors of the F_2 symmetry type for the group $O(T_d)$

A_1	A_2	E	F_1	F_2
$V^{2(0,A_1)}$	$V^{6(6,A_2)}$	$V^{2(2,E)}$	$V^{3(3,F_1)}$	$V^{1(1,F_2)}$
$V^{3(3,A_1)}$		$V^{4(4,E)}$	$V^{4(4,F_1)}$	$V^{2(2,F_2)}$
$V^{4(4,A_1)}$			$V^{5(5,F_1)}$	$V^{3(3,F_2)}$

theory. The GFs and IBs thus obtained are listed in table 6.

5. Generating functions satisfying the diagonality condition

Here we shall generalize the GF method to obtain the GFs for a number of linearly independent invariant and covariant operators of a given degree and satisfying the diagonality condition [33].

Denote the representation spanned by all annihilation operators by Γ. Then the representation spanned by the creation operators is Γ^*. In physically reasonable problems usually $\Gamma=\Gamma^*$. Following the standard recipes of invariant theory the GF for invariants constructed both from the creation and annihilation operators can be calculated as

$$g(A_1, \Gamma\oplus\Gamma^*; \lambda, \mu) = \sum_X g(X, \Gamma; \lambda)\, g(X, \Gamma^*; \mu). \tag{10}$$

Here, the sum is carried over all irreducible representations of X of G. The GF (10) is the rational function in two auxiliary variables λ and μ. It can be expanded in a power series of the form

$$g(A_1, \Gamma\oplus\Gamma^*; \lambda, \mu) = \sum_{\Omega_1,\Omega_2} b_{\Omega_1\Omega_2}\lambda^{\Omega_1}\mu^{\Omega_2}. \tag{11}$$

To take into account the diagonality condition one has to extract from the expansion (11) all terms with $\Omega_1=\Omega_2$,

$$g^{\mathrm{diag}}(A_1, \Gamma\oplus\Gamma^*; \lambda\mu) = \sum_{\Omega} b_{\Omega\Omega}(\lambda\mu)^{\Omega}. \tag{12}$$

We see that the GF for invariants satisfying the diagonality condition, diagonal GF, depends only on one auxiliary variable, $\lambda\mu$. To stress this fact and to simplify the forthcoming formulae we shall use for this variable a special designation: $\lambda\mu\equiv\xi$. The GF (12) may be transformed into a rational function of canonical form admitting the usual algebraic interpretation. As was already explained in section 2, care should be taken in using such interpretation for constructing the IB. We give below the GFs for several typical vibrational problems.

5.1. Totally symmetric vibrational operators

The image, G*, of any group in its totally symmetric representation is C_1. The same image arises for the symmetry group of H_{eff} in the case of n degrees of freedom transforming according to the same irreducible one-dimensional real representation.

In this case there exists only a GF for invariants which, for creation or annihilation operators, has the form

$$g(A, nA; \lambda) = (1-\lambda)^{-n}. \tag{13}$$

Table 6
Generating functions and basic invariants for the two-dimensional vibrational problem. Operators, J_α ($\alpha=x, y, z$), are taken as the initial ones. Here: LCD is the largest common divisor; $Z_k=1/(1-t^k)$; { } is symmetrizer; $\alpha\neq\beta\neq\gamma$

G*	Symmetry of J_α operators	Generating function	Basic invariants	
			denominator	numerator
C_1	3A	Z_1^3	$J_\alpha, J_\beta, J_\gamma$	–
C_2	A⊕2B	$(1+t^2)Z_1Z_2^2$	J_α^2, J_β, J^2	$\{J_\alpha J_\gamma\}$
D_2	$B_1\oplus B_2\oplus B_3$	$(1+t^3)Z_2^3$	$J_\alpha^2, J_\beta^2, J^2$	$\{J_\alpha J_\beta J_\gamma\}$
C_k	$\Gamma_0\oplus\Gamma_m\oplus\Gamma_m^*$	$(1+t^2+\ldots+t^{2k-2})Z_1Z_k^2$	$J_z, J_+^k+J_-^k,$	$J^2, J^4, \ldots, J^{2k-2}$
$k\geq 3$	$\mathrm{LCD}(m,k)=1$		$\mathrm{i}(J_+^k-J_-^k)$	
D_k	$A_2\oplus E_m$	$(1+t^{k+1})Z_2^2Z_k$	$J^2, J_z^2,$	$\mathrm{i}\{J_z(J_+^k-J_-^k)\}$
$k\geq 3$	$\mathrm{LCD}(m,k)=1$		$J_+^k+J_-^k$	

The GF for invariants constructed from both creation and annihilation operators without taking into account the diagonality condition is given by

$$g(\mathrm{A}, n\mathrm{A}\oplus n\mathrm{A}; \lambda, \mu) = [(1-\lambda)(1-\mu)]^{-n}. \quad (14)$$

Transformation of (14) into the diagonal form gives the following result

$$g^{\mathrm{diag}}(\mathrm{A}, n\mathrm{A}\oplus n\mathrm{A}; \xi) = \frac{1}{(1-\xi)^{2n-1}} \sum_{k=0}^{k=n-1} \left(\frac{(n-1)!}{k!(n-k-1)!}\right)^2 \xi^k. \quad (15)$$

Particular realizations of (15) for low n values are

$$g^{\mathrm{diag}}(\mathrm{A}, 2\mathrm{A}\oplus 2\mathrm{A}; \xi) = (1+\xi)/(1-\xi)^3, \quad (16a)$$

$$g^{\mathrm{diag}}(\mathrm{A}, 3\mathrm{A}\oplus 3\mathrm{A}; \xi) = (1+4\xi+\xi^2)/(1-\xi)^5, \quad (16b)$$

$$g^{\mathrm{diag}}(\mathrm{A}, 4\mathrm{A}\oplus 4\mathrm{A}; \xi) = (1+9\xi+9\xi^2+\xi^3)/(1-\xi)^7. \quad (16c)$$

5.2. Two-dimensional vibrational problem

The procedure similar to that presented above may be easily realized for any two-dimensional vibrational problem. All diagonal GFs possible in this case and the corresponding IBs are listed in table 7. We note that the GFs thus obtained may be easily deduced from the corresponding CFs given in table 6 by multiplying them by $(1+\xi)$. This is due to the fact, mentioned already in section 4, that any invariant operator satisfying the diagonality condition in the two-mode case may always be written in the form (9). The multiplication by the $(1+\xi)$ factor corresponds to the introduction of new numerator invariants, J and JI_m $(m=K+1, ..., K+L)$, where invariants, I_m, are the old numerator invariants, in addition to those listed in table 6. It should be stressed that the GFs thus obtained may not have the simplest possible form. It is clear that if an IB listed in table 6 includes J^2 as a denominator invariant, then one may simply use J as a denominator invariant instead of introducing the additional numerator invariants. The equivalent statement is that one may divide in this case both the numerator and denominator of the GF by $(1-\xi)$.

5.3. GFs for three-dimensional vibrational problem

The direct application of the procedure described at the beginning of this section enables us to calculate the diagonal GFs and for three-dimensional vibrational problems. In tables 8, 9, and 10 we give some diagonal GFs for invariants and covariants. The method of obtaining the diagonal GFs for covariants is the same as that for the invariants.

The diagonal GFs for invariants and covariants satisfy the relation

$$\sum_{\mathrm{X}} [\mathrm{X}] g^{\mathrm{diag}}(\mathrm{X}, \Gamma\oplus\Gamma; \xi) = g^{\mathrm{diag}}(\mathrm{A}, [\Gamma]\mathrm{A}\oplus[\Gamma]\mathrm{A}; \xi), \quad (17)$$

where $[\mathrm{X}]$ is the dimension of the irreducible representation X and the sum is carried over all irreducible representations of the image, G*. Formula (17) is the generalization of the known expression

$$\sum_{\mathrm{X}} [\mathrm{X}] g(\mathrm{X}, \Gamma; \lambda) = (1-\lambda)^{-n} \quad (18)$$

Table 7
Generating functions and basic invariants for the two-dimensional vibrational problem. The a_1, a_2, a_1^+, a_2^+ operators are taken as the initial ones. The diagonality condition is assumed. Here: LCD is the largest common divisor; $\xi=\lambda\mu$; $Z_k=1/(1-\xi^k)$; { } is symmetrizer

G*	Symmetry of $a_i^+ a_j$	Generating function	Basic invariants	
			denominator	numerator
C_1	4A	$(1+\xi)Z_1^3$	$J_\alpha, J_\beta, J_\gamma$	J
C_2	2A⊕2B	$(1+\xi^2)Z_1^2Z_2$	J_α^2, J_β, J	$\{J_\alpha J_\gamma\}$
D_2	A⊕B_1⊕B_2⊕B_3	$(1+\xi^3)Z_1Z_2^2$	J_α^2, J_β^2, J	$\{J_\alpha J_\beta J_\gamma\}$
C_k	$2\Gamma_0\oplus\Gamma_m\oplus\Gamma_m^*$	$(1+\xi+...+\xi^{2k-1})Z_1Z_k^2$	$J_z, J_+^k+J_-^k$,	$J, J^2, ..., J^{2k-1}$
$k\geqslant 3$	LCD$(m,k)=1$		$\mathrm{i}(J_+^k-J_-^k)$	
D_k	$A_1\oplus A_2\oplus E_m$	$(1+\xi^{k+1})Z_1Z_2Z_k$	J, J_z^2,	$\mathrm{i}\{J_z(J_+^k-J_-^k)\}$
$k\geqslant 3$	LCD$(m,k)=1$		$J_+^k+J_-^k$	

Table 8
Generating functions for invariants and covariants of the Γ_f type for the problem with three nondegenerate vibrations under diagonality condition. Here: $\xi=\lambda\mu$; $i=1, 2, 3$; $Z=(1-\xi)^3(1-\xi^2)^2$

G*	Γ_f	Generating function
C_1	A	$(1+4\xi+\xi^2)/(1-\xi)^5$
C_2	A	$(1+2\xi+6\xi^2+2\xi^3+\xi^4)/Z$
	B	$(4\xi+4\xi^2+4\xi^3)/Z$
D_2	A	$(1+4\xi^2+\xi^4)/Z$
	B_i	$(2\xi+2\xi^2+2\xi^3)/Z$

for the GFs without any additional requirements.

We note also that the number of numerator covariants of the type Γ is equal to the number of the numerator invariants (including 1) multiplied by $[\Gamma]$.

6. Integrity bases

The GFs listed in tables 8, 9, and 10 simplify the search of the corresponding IBs. Nevertheless, this problem remains individual for the most part of the images, especially if one wants to find the minimal number of basic invariants. We give in this section the IBs for vibrational problems with three nondegenerate vibrations (images C_1, C_2, D_2) and for those whose image is O group (triply degenerate vibrations of O, T_d, and O_h groups). The results are presented in tables 11 and 12. We do not know a systematic procedure for deriving the IBs. Moreover, the IB may be presented in a variety of forms [13]. The correctness of the IBs listed in tables 11 and 12 was verified by checking whether they really give all the linearly independent terms of a given degree, or not. The check was based on a straightforward calculation of the rank of the matrix transforming the operators of a given degree obtained by the IB method into that obtained by the method (A) described in section 4.

7. Conclusions

We have studied the general structure of the effective Hamiltonians for vibrational polyads. The use of the group image concept enables us to reduce considerably the number of different cases to study. The invariant theory (in particular the generating function method) has been used to find the general algebraic structure of the IBs for the problems considered. The explicit construction of the IBs for several important cases has been given. The results obtained permit us in fact to make the first step in the general study of qualitative features of the dynamics of molecular vi-

Table 9
Generating functions for invariants and covariants of the Γ_f type for the problem with triply degenerate vibrations under diagonality condition. Here: $\xi=\lambda\mu$; $i, j=1, 2$; $i\neq j$. In parentheses under the group symbol, the irreducible representation for annihilation operators is given

G*	Γ_f	Generating function
T	A	$(1+5\xi^3+5\xi^4+\xi^7)/Z_T$
(F)	E_i	$(\xi+3\xi^2+2\xi^3+2\xi^4+3\xi^5+\xi^6)/Z_T$
	F	$(2\xi+6\xi^2+10\xi^3+10\xi^4+6\xi^5+2\xi^6)/Z_T$
		$Z_T=(1-\xi)(1-\xi^2)^3(1-\xi^3)$
O	A_1	$(1+2\xi^3+3\xi^4+3\xi^5+2\xi^6+\xi^9)/Z_O$
(F_i)	A_2	$(\xi^2+3\xi^3+2\xi^4+2\xi^5+3\xi^6+\xi^7)/Z_O$
	E	$(\xi+3\xi^2+3\xi^3+5\xi^4+5\xi^5+3\xi^6+3\xi^7+\xi^8)/Z_O$
	F_1	$(\xi+2\xi^2+6\xi^3+9\xi^4+9\xi^5+6\xi^6+2\xi^7+\xi^8)/Z_O$
	F_2	$(\xi+4\xi^2+6\xi^3+7\xi^4+7\xi^5+6\xi^6+4\xi^7+\xi^8)/Z_O$
		$Z_O=(1-\xi)(1-\xi^2)^2(1-\xi^3)(1-\xi^4)$
I	A	$(1+\xi^4+2\xi^5+4\xi^6+2\xi^7+\xi^8+\xi^{12})/Z_I$
(F_i)	F_i	$(\xi+2\xi^3+4\xi^4+7\xi^5+8\xi^6+7\xi^7+4\xi^8+2\xi^9+\xi^{11})/Z_I$
	F_j	$(\xi^2+3\xi^3+4\xi^4+7\xi^5+8\xi^6+7\xi^7+4\xi^8+3\xi^9+\xi^{10})/Z_I$
	G	$(2\xi^2+5\xi^3+6\xi^4+7\xi^5+8\xi^6+7\xi^7+6\xi^8+5\xi^9+2\xi^{10})/Z_I$
	H	$(\xi+3\xi^2+4\xi^3+8\xi^4+9\xi^5+10\xi^6+9\xi^7+8\xi^8+4\xi^9+3\xi^{10}+\xi^{11})/Z_I$
		$Z_I=(1-\xi)(1-\xi^2)(1-\xi^3)(1-\xi^4)(1-\xi^5)$

Table 10
Generating functions for invariants for a three-dimensional vibrational problem (one nondegenerate and one doubly degenerate vibration) under the diagonality condition. Here: $\xi=\lambda\mu$; $Z=(1-\xi)^2(1-\xi^2)^2(1-\xi^n)$; Γ_i is symmetry of the bilinear combinations $a_i^+ a_j$ in G*

G*	Γ_i	Generating function
C_n $n\geqslant 3$, n odd	$3\Gamma_0\oplus 3\Gamma_1\oplus 3\Gamma_1^*$	$[1+\xi+\xi^2+\xi^3+\xi^n+\xi^{n+1}+\xi^{n+2}+\xi^{n+3}+4\xi^{(n+1)/2}+8\xi^{(n+3)/2}+4\xi^{(n+5)/2}]/Z$
C_n $n\geqslant 4$, n even	$3\Gamma_0\oplus 3\Gamma_1\oplus 3\Gamma_1^*$	$[1+\xi+\xi^2+\xi^3+\xi^n+\xi^{n+1}+\xi^{n+2}+\xi^{n+3}+2\xi^{n/2}+6\xi^{n/2+1}+6\xi^{n/2+2}+2\xi^{n/2+3}]/Z$
D_n $n\geqslant 3$, n odd	$3A_1\oplus 3E_1$	$[1+\xi^2+\xi^{n+1}+\xi^{n+3}+2\xi^{(n+1)/2}+4\xi^{(n+3)/2}+2\xi^{(n+5)/2}]/Z$
D_n $n\geqslant 4$, n even	$3A_1\oplus 3E_1$	$[1+\xi^2+\xi^{n+1}+\xi^{n+3}+\xi^{n/2}+3\xi^{n/2+1}+3\xi^{n/2+2}+3\xi^{n/2+3}]/Z$

brators including several degrees of freedom. Our recent work [38–43] has shown the existence of several types of qualitative effects in the dynamical behaviour of finite particle systems. In fact, the systems studied were reduced to the case of a phase space spanned by two variables. Generalization to problems with more variables requires a suitable general form of the effective Hamiltonian. This is just the problem solved here for the vibrational polyads with several degrees of freedom.

Table 11
Integrity bases for three-dimensional vibrational problem with three nondegenerate vibrations. Variables λ_i (μ_i) correspond to the annihilation (creation) vibrational operators

G*	Basic invariants	
	denominator	numerator
C_1	$I_1=\lambda_1\mu_1$	$I_6=\lambda_1\mu_2-\lambda_2\mu_3+\lambda_3\mu_1$
	$I_2=\lambda_2\mu_2$	$I_7=\lambda_1\mu_2-\lambda_3\mu_1$
	$I_3=\lambda_3\mu_3$	$I_8=\lambda_1\mu_3-\lambda_2\mu_1+\lambda_3\mu_2$
	$I_4=\lambda_1\mu_2+\lambda_2\mu_3+\lambda_3\mu_1$	$I_9=\lambda_1\mu_3-\lambda_3\mu_2$
	$I_5=\lambda_1\mu_3+\lambda_2\mu_1+\lambda_3\mu_2$	$I_{10}=\lambda_1^2\mu_3\mu_2+\lambda_2^2\mu_1\mu_3+\lambda_3^2\mu_1\mu_2-\lambda_1\lambda_2\mu_3^2-\lambda_1\lambda_3\mu_2^2-\lambda_2\lambda_3\mu_1^2$
C_2	$I_1=\lambda_1\mu_1$	$I_6=\lambda_1\mu_2$
	$I_2=\lambda_2\mu_2$	$I_7=\lambda_2\mu_1$
	$I_3=\lambda_3\mu_3$	$I_8=\lambda_2^3\mu_1\mu_3^3-\lambda_2\lambda_3^3\mu_1^3$
	$I_4=\lambda_1^2\mu_2^2+\lambda_2^2\mu_3^2+\lambda_3^2\mu_1^2$	$I_9=\lambda_1^3\mu_2\mu_3^3-\lambda_1\lambda_3^3\mu_2^3$
	$I_5=\lambda_1^2\mu_3^2+\lambda_2^2\mu_1^2+\lambda_3^2\mu_2^2$	$I_{10}=\lambda_1^2\mu_2^2-\lambda_2^2\mu_3^2+\lambda_3^2\mu_1^2$
		$I_{11}=\lambda_1^2\mu_2^2-\lambda_3^2\mu_1^2$
		$I_{12}=\lambda_1^2\mu_3^2-\lambda_2^2\mu_1^2+\lambda_3^2\mu_2^2$
		$I_{13}=\lambda_1^2\mu_3^2-\lambda_3^2\mu_2^2$
		$I_{14}=\lambda_3^2\mu_1\mu_2$
		$I_{15}=\lambda_1\lambda_2\mu_3^2$
		$I_{16}=\lambda_1^4\mu_2^2\mu_3^2+\lambda_2^4\mu_1^2\mu_3^2+\lambda_3^4\mu_1^2\mu_2^2-\mu_1^4\lambda_2^2\lambda_3^2-\mu_2^4\lambda_1^2\lambda_3^2-\mu_3^4\lambda_1^2\lambda_2^2$
D_2	$I_1=\lambda_1\mu_1$	$I_6=\lambda_1^2\mu_2^2-\lambda_2^2\mu_3^2+\lambda_3^2\mu_1^2$
	$I_2=\lambda_2\mu_2$	$I_7=\lambda_1^2\mu_2^2-\lambda_3^2\mu_1^2$
	$I_3=\lambda_3\mu_3$	$I_8=\lambda_1^2\mu_3^2-\lambda_2^2\mu_1^2+\lambda_3^2\mu_2^2$
	$I_4=\lambda_1^2\mu_2^2+\lambda_2^2\mu_3^2+\lambda_3^2\mu_1^2$	$I_9=\lambda_1^2\mu_3^2-\lambda_3^2\mu_2^2$
	$I_5=\lambda_1^2\mu_3^2+\lambda_2^2\mu_1^2+\lambda_3^2\mu_2^2$	$I_{10}=\lambda_1^4\mu_2^2\mu_3^2+\lambda_2^4\mu_1^2\mu_3^2+\lambda_3^4\mu_1^2\mu_2^2-\mu_1^4\lambda_2^2\lambda_3^2-\mu_2^4\lambda_1^2\lambda_3^2-\mu_3^4\lambda_1^2\lambda_2^2$

Table 12
Integrity basis for F_2 vibrations of $O(T_d)$ symmetry group under diagonality condition. The invariants listed here correspond to the generating functions in table 9

Denominator invariants	Numerator invariants
$\begin{pmatrix}100\\100\end{pmatrix}$, $\begin{pmatrix}110\\110\end{pmatrix}$,	$\begin{pmatrix}300\\120\end{pmatrix}_{\pm}$, $\begin{pmatrix}301\\121\end{pmatrix}_{\pm}$, $\begin{pmatrix}400\\022\end{pmatrix}_{-}$,
$\begin{pmatrix}111\\111\end{pmatrix}$, $\begin{pmatrix}200\\020\end{pmatrix}$,	$\begin{pmatrix}302\\122\end{pmatrix}_{-}$, $\begin{pmatrix}410\\032\end{pmatrix}_{\pm}$, $\begin{pmatrix}411\\033\end{pmatrix}_{\pm}$,
$\begin{pmatrix}400\\022\end{pmatrix}_{+}$	$\left[\begin{pmatrix}702\\144\end{pmatrix}_{+} - \begin{pmatrix}612\\054\end{pmatrix}_{+}\right]$

$$\begin{pmatrix}abc\\pqr\end{pmatrix} = \lambda_1^q\lambda_2^b\lambda_3^c\mu_1^p\mu_2^q\mu_3^r + \lambda_2^q\lambda_3^b\lambda_1^c\mu_2^p\mu_3^r\mu_1^q + \lambda_3^q\lambda_1^b\lambda_2^c\mu_3^p\mu_1^r\mu_2^q \cdot$$

$$+\lambda_3^q\lambda_2^b\lambda_1^c\mu_3^p\mu_2^q\mu_1^r + \lambda_2^q\lambda_1^b\lambda_3^c\mu_2^p\mu_1^q\mu_3^r + \lambda_1^q\lambda_3^b\lambda_2^c\mu_1^p\mu_3^q\mu_2^r$$

$$\begin{pmatrix}abc\\pqr\end{pmatrix}_{\pm} = \begin{pmatrix}abc\\pqr\end{pmatrix} \pm \begin{pmatrix}pqr\\abc\end{pmatrix}$$

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References

[1] M.S. Child and L. Halonen, Advan. Chem. Phys. 57 (1984) 1.
[2] I. Mills and A.G. Robiette, Mol. Phys. 56 (1985) 743.
[3] F. Michelot and J. Moret-Bailly, J. Phys. (Paris) 48 (1987) 51.
[4] C. Patterson, J. Chem. Phys. 83 (1985) 4618.
[5] M.E. Kellman, J. Chem. Phys. 83 (1985) 3843.
[6] R.D. Levine and J.L. Kinsey, J. Phys. Chem. 90 (1986) 3653.
[7] M.E. Kellman and E.D. Lynch, J. Chem. Phys. 85 (1986) 7216.
[8] K. Stefanski and E. Pollak, J. Chem. Phys. 87 (1987) 1079.
[9] R.H. Page, Y.R. Shen and Y.J. Lee, Phys. Rev. Letters 59 (1987) 1293.
[10] C.D. Cantrell, in: Multiphoton processes, eds. J.H. Eberly and P. Lambropoulos (Wiley, New York, 1978) p. 307.
[11] R. Gilmore and J.R. Draayer, J. Math. Phys. 26 (1985) 3053.
[12] J. Patera and P. Winternitz, J. Chem. Phys. 65 (1976) 2725.
[13] R.P. Bickerstuff and B.G. Wybourne, J. Phys. A 9 (1976) 1051.
[14] B. Meyer, Can. J. Math. 6 (1954) 135.
[15] H. Weyl, The classical groups (Princeton Univ. Press, Princeton, 1953).
[16] A.J.M. Spencer, in: Continuum physics, Vol. 1, part 3 (Academic Press, New York, 1971).
[17] L. Michel, in: Regards sur la physique contemporaire (CNRS, Paris, 1980) p. 157.
[18] J.C. Toledano, L. Michel, P. Toledano and E. Brezin, Phys. Rev. B 31 (1985) 7171.
[19] A. Schmelzer and J.N. Murrell, Intern. J. Quantum Chem. 28 (1985) 287.
[20] L. Michel and J. Morzymas, Lect. Notes Phys. 79 (1977) 447.
[21] M.V. Jaric, L. Michel and R.T. Sharp, J. Phys. (Paris) 45 (1984) 1.
[22] Yu.A. Izyumov and V.N. Syromyatnikov, Phase transitions and symmetry of crystals (Nauka, Moscow, 1984) (in Russian).
[23] T. Molien, Preuss Akad. Wiss. (1897) 1152.
[24] W. Burnside, Theory of groups of finite order (Cambridge Univ. Press, Cambridge, 1911).
[25] T.A. Springer, Lect. Notes Math. 585 (1977).
[26] F.J. MacWilliams and N.S.A. Sloane, The theory of error-correcting codes (Reidel, Dordrecht, 1977) ch. 19.
[27] R.P. Stanley, Bull. Am. Math. Soc. 1 (1979) 475.
[28] J. Patera and R.T. Sharp, J. Math. Phys. 19 (1978) 2362.
[29] P.E. Desmier and R.T. Sharp, J. Math. Phys. 20 (1979) 74.
[30] M.V. Jaric and J.L. Birman, J. Math. Phys. 18 (1977) 1456.
[31] M.V. Jaric and J.L. Birman, J. Math. Phys. 18 (1977) 1459.
[32] M.V. Jaric, J. Math. Phys. 25 (1984) 3363.
[33] R.M. Asherova, V.B. Pavlov-Verevkin, Yu.F. Smirnov and B.I. Zhilinskii, FEI preprint (1987).
[34] J. Schwinger, in: Quantum theory of angular momentum, eds. L.C. Biedenharn and H. van Dam (Academic Press, New York, 1965) p. 229.
[35] H.S.M. Coxeter and W.O.J. Moser, Generators and relations for discrete groups (Springer, Berlin, 1972).
[36] M.E. Kellman, Chem. Phys. Letters 99 (1983) 437.
[37] S. Okubo, J. Math. Phys. 16 (1975) 528.
[38] I.M. Pavlichenkov and B.I. Zhilinskii, Chem. Phys. 100 (1985) 339.
[39] B.I. Zhilinskii and D.A. Sadovskii, Opt. i Spektrosopiya 61 (1986) 481.
[40] B.I. Zhilinskii and I.M. Pavlichenkov, Zh. Eksp. Teor. Fiz. 92 (1987) 387.
[41] I.M. Pavlichenkov and B.I. Zhilinskii, Ann. Phys., to be published.
[42] V.B. Pavlov-Verevkin and B.I. Zhilinskii, Khim. Fiz. 6 (1987) 1459.
[43] V.B. Pavlov-Verevkin and B.I. Zhilinskii, Opt. i Spektroskopiya 64 (1988) 46.