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Integrity bases for covariants of tetrahedral XY_4 molecules. Application to the electric dipole moment surface

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Techniques of invariant theory such as Molien generating functions and integrity bases offer mathematical tools for the efficient construction of symmetry–adapted polynomials in the symmetrized coordinates of a molecular system. The present article is the prolongation of our previous work [P. Cassam-Chenaï and F. Patras, J. Math. Chem., 44(4), 938–966 (2008).] to the case of polynomials that transform as a non–totally symmetric irreducible representation of the symmetry group G of the molecule. Such a covariant representation occurs with electric or magnetic properties, for example with the electric dipole moment surface. The symmetrized coordinates span an initial reducible representation from which polynomials transforming as an irreducible representation are built. The number of linearly independent polynomials of degree k within this final representation is given by the coefficient of degree k in the Taylor expansion of the associated Molien function. This generating function is built from combination of elementary generating functions where both the initial and final representations are irreducible. In parallel, Clebsch–Gordan coefficients of the symmetry group G recursively couples the corresponding elementary integrity bases in order to build the integrity bases for the initial representation associated to symmetrized coordinates. The method is illustrated in detail on XY_4 type of molecules for which the explicit integrity bases for the five final irreducible representations are given.

I. INTRODUCTION

Microwave or infrared synthetic spectrum generation requires the knowledge of the potential energy surface (PES) and of the electric dipole moment surface (EDMS) of the molecule under study. These two functions of internal coordinates do not have a known analytic expression. This problem is often encountered in quantum chemistry or computational spectroscopy and a typical strategy is to expand these functions on a set of appropriate analytical functions. The expansion coefficients are then determined empirically or by fitting over experimental or theoretical data. The molecular symmetry helps to simplify the problem[1–5] and favors the introduction of symmetry–adapted coordinates when the function to be expanded transforms according to an irreducible representation of the symmetry group G of the molecule. In particular, the PES transforms as the totally symmetric (also called trivial) irreducible representation of the group G while the components of the EDMS may carry a non–trivial representation of the group.

The set of symmetrized internal coordinates usually spans a reducible representation called the initial representation Γ_i. Symmetry–adapted polynomials in these variables are then considered. The polynomials that transform according to the final irreducible representation Γ_f are called Γ_f–covariant polynomials.[6] A Γ_f–covariant polynomial is called an invariant polynomial if the Γ_f representation is the trivial representation of the group.

The projector or Reynolds operator is a standard method of group theory to generate invariant and Γ_f–covariant polynomials. Marquardt[7] and Schwenke[8] applied this technique to compute the terms that appear in the expansion of the PES of methane. The method for the construction of invariants is applicable to irreducible representations (irreps.) of dimension higher than one through the introduction of projection operators together with transfer operators, see Hamermesh,[9] Bunker,[4] Lomont,[10] and Taylor.[11] The group–theoretical methods based on projector operators are inherently inefficient because they ignore the number of linearly independent symmetry-adapted polynomials of a given degree k. So, in order to obtain a complete set, they have to consider all possible starting polynomial "seeds", usually a basis set of monomials. The projection of the latters often lead to the null polynomial or to a useless linear combination of already known symmetry-adapted polynomials. Furthermore, the dimension of the space of symmetry-adapted polynomials becomes rapidly formidable even at modest k and the list of polynomials to tabulate becomes unnecessarily gigantic.

Another technique of construction of Γ_f–covariant polynomials is based on the Clebsch–Gordan coefficients of group G. A great deal of work has been dedicated in particular to the cubic group.[12–15] The coupling with the Clebsch–Gordan coefficients of two polynomials give a polynomial of higher degree and the set of symmetry–adapted polynomials is built degree by degree. All possible couplings between (vector) basis sets of polynomials of lower degrees must be considered to insure that one

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gets a complete list. As in the projector method, this results in many linearly dependent polynomials of a given degree k that have to be eliminated.

The drawbacks of the two approaches evoked above are circumvented by the theory of algebraic invariants. In particular, the coefficients of the Taylor expansion of the Molien generating function[16,17] give information about the number of linearly independent polynomials of a given degree k carrying a given irreducible representation. The introduction of invariant theory in quantum chemistry can be traced back to the works of Murrell *et al.*[18,19]. Followers include Collins and Parsons,[20] Ischtwan and Peyerimhoff,[21] and, more recently, Braams and Bowman.[22] However, these studies were only concerned with the totally symmetric representation in relation to the expansion of a PES. Braams and Bowman did consider expansions of an EDMS but they reduced the problem to the totally symmetric case by restricting themselves to a subgroup of the molecular point group, which is not optimal.

An integrity basis for the Γ_f–covariant polynomials is a finite set of polynomials with the special property that any Γ_f–covariant uniquely decomposes as a polynomial function in the elements of the integrity basis. The integrity basis contains two partitions.[16,23] The first partition contains the so–called denominator or primary polynomials.[16,24] They are invariant polynomials and their corresponding power in the decomposition of a Γ_f–covariant can be any natural integer. The second subset contains the numerator or secondary polynomials. They transform as the Γ_f representation and their corresponding power can only be zero or one. An integrity basis being given, generating a list of linearly independent, symmetry-adapted polynomials of an arbitrarily high degree is a simple task requiring only multiplications between the finite number of basis polynomials. This is in contrast with techniques already described, which first consider large sets of polynomials and then project out linearly dependent subsets and/or polynomials that do not carry the proper irreducible representation.

Our previous paper[17] considered the complete permutation–rotation–inversion group of a XY_4 molecule. An integrity basis for the invariant polynomials was computed. The calculation was decomposed into two steps and this decomposition was an important feature of the method. First, we were dealing with the rotation–inversion group $O(3)$ and in a second step with the finite permutation group. The structure of covariants for the rotation–inversion group is interesting on its own, since it raises specific problems related to the fact that the modules of covariants are not necessarily free for reductive continuous groups such as $O(2)$ or $O(3)$.[23,25,26] This is a remarkable difference with respect to the algebraic structure of invariants. Forthcoming articles will be devoted to the study of covariant modules of the $O(2)$ and $O(3)$ groups.[23,27]

The focus of the present article is on the Γ_f–covariants built from symmetrized coordinates in the tetrahedral T_d point group. As a matter of fact, various types of such coordinates have appeared in the literature for this system that are amenable to our treatment. We can mention curvilinear internal displacements (bond lengths and interbond angles),[28,29] Cartesian normal coordinates,[28,30–34] symmetrized coordinates based on Morse coordinates on Radau vectors for stretching modes and cosines of valence bond angles for bending modes,[8] haversines of bond angles,[35] cosines of valence bond angles times functions of bond lengths,[36] symmetrized coordinates based on bond lengths, interbond angles and torsion angles,[15] or interbond angles and bond lengths times a gaussian exponential factor.[37]

The purpose of the present article is to show on the explicit exemple of a XY_4 molecule that the techniques of invariant theory that were used to obtain a polynomial basis set for totally symmetrical quantities[17] are straightforwardly extended to quantities transforming according to an arbitrary irreducible representation Γ_f of the symmetry group G. This is useful to obtain very efficiently a basis set of F_2–symmetry-adapted polynomials up to any arbitrary degree, for example. Such a basis can be used to fit the EDMS of methane. The F_1–covariants might be relevant to fit the magnetic dipole moment surface (MDMS) while the E–covariants might be required for the components of the quadrupole moment surfaces. Various already existing algorithms could theoretically be used for the same purpose such as those associated to Gröbner basis computations (see e.g. Ref.[38]). However, on the one hand, existing methods of computational invariant theory[24,39,40] are usually implemented in available computer codes for invariants only, and on the other hand, they do not seem to be able to treat high–dimensional problems efficiently for intrinsic complexity reasons, even in the case of invariants.

The article is organized as follows. In the next section, we recall fundamental results of invariant theory. Then, we show how the integrity basis of Γ_f–covariant polynomials in the T_d point group can be constructed recursively for XY_4 molecules, $\Gamma_f \in \{A_1, A_2, E, F_1, F_2\}$. The resulting minimal generating families of symmetry–adapted functions are listed in supplementary materials[41]. In conclusion, we emphasize the points of our approach which are general and those that are specific to the example chosen as an illustration.

II. SYMMETRY–ADAPTATION TO A FINITE GROUP G

The theoretical framework to describe invariants in polynomial algebras under finite group actions is well developped, both in mathematics and in chemical physics. Classical references on the subject in mathematics are the books by Benson[42] and Stanley[43]. Schmelzer and Murrell[19] have had a pioneering influence as far as the construction of a PES is concerned. Refs.[16,44] give an overview of the various possible applications to chemistry and physics.

We rely in the present section on a fundamental result of commutative algebra and representation theory stating that G–invariant and G–covariant polynomials have a general decomposition. We refer to Ref.[43] for further details and proofs regarding this result and other properties of finite group actions on polynomial algebras.

A. Hironaka decomposition

Let $\mathcal{P}$ denote the algebra of polynomials in k coordinates, $Q_1, \ldots, Q_k$, for the field of complex numbers, $\mathcal{P} = \bigoplus_{n\geq 0} \mathcal{P}_n$, where $\mathcal{P}_n$ is the vector space of polynomials of degree n. We assume that the finite group G acts linearly on the vector space $\mathcal{Q} =< Q_1, \ldots, Q_k >$ spanned by $Q_1, \ldots, Q_k$. This action extends naturally to $\mathcal{P}$.

Let $\mathcal{P}^{\Gamma_f}$ be the vector subspace of polynomials transforming as the irreducible representation Γ_f. We write $[\Gamma_f]$ for the dimension of Γ_f. The group action preserving polynomial degrees, we have the decomposition $\mathcal{P}^{\Gamma_f} = \bigoplus_{n\geq 0} \mathcal{P}_n^{\Gamma_f}$, where $\mathcal{P}_n^{\Gamma_f} = \mathcal{P}^{\Gamma_f} \cap \mathcal{P}_n$ is the vector space of Γ_f-covariant polynomials of degree n for G.

When the representation is said "degenerate", that is to say, when $[\Gamma_f] > 1$, it is convenient to assume for forthcoming developments that the representation Γ_f has a distinguished basis $\psi_1, ..., \psi_{[\Gamma_f]}$. The polynomials P in $\mathcal{P}^{\Gamma_f}$ can then be decomposed further as a sum of polynomials,

$$P = \sum_{i=1}^{[\Gamma_f]} P_i, \tag{1}$$

each term behaving as a base function ψ_i, see e.g. Ref.[44] (Chap. 3). We will say that P_i is of type Γ_f, i and write $\mathcal{P}^{\Gamma_f} = \bigoplus_{i=1}^{[\Gamma_f]} \mathcal{P}^{\Gamma_f,i}$ the corresponding decomposition of the vector space of Γ_f–covariant polynomials.

An important mathematical result is that there exists k basic invariant polynomials $f_1, \ldots, f_k$ and a finite number, p_{Γ_f}, of Γ_f-covariant polynomials, $g_1^{\Gamma_f}, \ldots, g_{p_{\Gamma_f}}^{\Gamma_f}$, such that

$$\mathcal{P}^{\Gamma_f} = \mathbb{C}[f_1, ..., f_k] g_1^{\Gamma_f} \oplus \cdots \oplus \mathbb{C}[f_1, ..., f_k] g_{p_{\Gamma_f}}^{\Gamma_f}, \tag{2}$$

where $\mathbb{C}[f_1, ..., f_k]$ is the algebra spanned by the $f_1, \ldots, f_k$ polynomials. Such a decomposition is sometimes referred to as an Hironaka decomposition, and defines a so-called Cohen-Macaulay module. In the particular case where Γ_f is the trivial representation (so that Γ_f–covariants are simply invariants), this result shows that $\mathcal{P}^{\Gamma_f} \equiv \mathcal{P}^G$ is a Cohen–Macaulay algebra. The f_i are called the "primary", "basic", or "fundamental" invariant basis polynomials, while the $g_j^{\Gamma_f}$ are called the Γ_f–covariant basis polynomials. The same set of primary invariants is used for all irreps.

It is convenient once again to take advantage of the decomposition Eq.(1). The Γ_f–covariant basis polynomials can be chosen as behaving as the basis functions ψ_i under the action of G. For each i, $1 \leq i \leq [\Gamma_f]$, there are $q_{\Gamma_f} = \frac{p_{\Gamma_f}}{[\Gamma_f]}$ Γ_f–covariant basis polynomials of type i. Let us assume that the first q_{Γ_f} Γ_f–covariant basis polynomials are of type 1: $g_1^{\Gamma_f,1}, ..., g_{q_{\Gamma_f}}^{\Gamma_f,1}$. We will then refer to the whole set $\{f_1, ..., f_k; g_1^{\Gamma_f,1}, ..., g_{q_{\Gamma_f}}^{\Gamma_f,1}\}$ as an integrity basis of the module $\mathcal{P}^{\Gamma_f,1}$ and to the particular set, $g_1^{\Gamma_f,1}, ..., g_{q_{\Gamma_f}}^{\Gamma_f,1}$, as the set of Γ_f–covariant basis polynomials of type 1. Once these polynomials have been constructed, universal formulas allow to construct partner families of Γ_f–covariant polynomials of arbitrary type $i > 1$, see e.g. Ref.[44] (Sect. 3-18).

The elements of an integrity basis can always be choosen homogeneous, and from now on, we will always assume that this homogeneity property holds. Even with this assumption, the number of basis polynomials is not determined by the above construction. However, for a given choice of primary invariants, the number of Γ_f–covariant basis polynomials and their degrees are fixed and determined by the so-called Molien series[45].

By definition, the Molien series, $M^G(\Gamma_f; \mathcal{Q}; t)$, associated to the representation of G on $\mathcal{Q}$ for Γ_f–covariants is

$$\begin{aligned} M^G(\Gamma_f; \mathcal{Q}; t) &= \frac{1}{[\Gamma_f]} \sum_{n\geq 0} \dim \mathcal{P}_n^{\Gamma_f} \; t^n \\ &= \sum_{n\geq 0} \dim \mathcal{P}_n^{\Gamma_f,i} \; t^n, \end{aligned} \tag{3}$$

where the second equality holds for all $i \in \{1, \cdots, [\Gamma_f]\}$, so in particular for $i = 1$. In other words, the coefficients of the Molien series, $\dim \mathcal{P}_n^{\Gamma_f,i}$, are the numbers of linearly independent Γ_f, i polynomials of degree n.

Suppose that $\{f_1, ..., f_k; g_1^{\Gamma_f,i}, ..., g_{q_{\Gamma_f}}^{\Gamma_f,i}\}$ is a given integrity basis, then it can be shown that, the corresponding Molien series can be cast in the following form:

$$M^G(\Gamma_f; \mathcal{Q}; t) = \frac{t^{\deg(g_1^{\Gamma_f,i})} + ... + t^{\deg(g_{q_{\Gamma_f}}^{\Gamma_f,i})}}{(1 - t^{\deg(f_1)}) \ldots (1 - t^{\deg(f_k)})}, \tag{4}$$

where $\deg(p)$ is the total degree of the multivariate polynomial p, (the degrees are not necessarily distinct in this expression). Hence, the common denomination of primary invariant basis polynomials as "denominator polynomials", and of covariant basis polynomials as "numerator polynomials". Once the degrees of the denominator invariants are given and the Molien series calculated, the number of Γ_f, i–covariant numerator polynomials of each degree is given by the corresponding coefficient of the polynomial $M^G(\Gamma_f; \mathcal{Q}; t) \cdot (1 - t^{\deg(f_1)}) \ldots (1 - t^{\deg(f_k)})$. The problem of generating $\mathcal{P}^{\Gamma_f,i}$ comes down to the computation of a complete set of such Γ_f, i–covariant numerator polynomials given a set of denominator invariants.

B. Recursive construction

We considered in the previous section the action of a finite group G on a polynomial algebra $\mathcal{P}$ over a vector space $\mathcal{Q}$. It is convenient to refine these results to the case where the linear representation of G, $\mathcal{Q}$, splits into a direct sum of representations, $\mathcal{Q} = \mathcal{Q}_{a_1} \oplus ... \oplus \mathcal{Q}_{a_n}$. We write $\mathcal{P}_{a_i}$ for the polynomial algebra generated by $\mathcal{Q}_{a_i}$, and write similarly with an a_i index the various objects and quantities associated to $\mathcal{Q}_{a_i}$. So, the related Molien series will be denoted $M^G(\Gamma_f; \mathcal{Q}_{a_i}; t)$. The polynomial algebra generated by partial direct sum up to the ith-component, $\mathcal{Q}^{[i]} := \mathcal{Q}_{a_1} \oplus ... \oplus \mathcal{Q}_{a_i}$, is written $\mathcal{P}^{[i]}$. We write $M^G\left(\Gamma_f; \mathcal{Q}^{[i]}; t\right)$ for the Molien series associated to Γ_f–covariants on $\mathcal{P}^{[i]}$.

Let us note $c^{\nu}_{\Gamma_\alpha,\Gamma_\beta}$ for the multiplicity of the irreducible representation ν in the direct (or Kronecker) product of the irreps. Γ_α and Γ_β. The generating function for a reducible, initial representation can be built by coupling generating function for irreps. of the group[16,46,47], see Equation (46) of Ref.[16], and Appendix. So, our Molien series being such generating functions, they can be built according to the following recursion formula: $\forall i \in \{2, \cdots, [\Gamma_f]\}$

$$M^G\left(\Gamma_f; \mathcal{Q}^{[i]}; t\right) = \sum_{\Gamma_\alpha,\Gamma_\beta} c^{\Gamma_f}_{\Gamma_\alpha,\Gamma_\beta} M^G\left(\Gamma_\alpha; \mathcal{Q}^{[i-1]}; t\right) M^G\left(\Gamma_\beta; \mathcal{Q}_{a_i}; t\right), \quad (5)$$

where the sum runs over all irreps Γ_α and Γ_β. In case of the T_d point group, $c^{\Gamma_f}_{\Gamma_\alpha,\Gamma_\beta} = 0$ or 1, see Ref.[1].

The same recursion principle can be used to construct an integrity basis for $\mathcal{P}^{\Gamma_f}$. Let $\{f_1, ..., f_k; g_1^{\Gamma_\alpha}, ..., g^{\Gamma_\alpha}_{p_{\Gamma_\alpha}}\}$ be an integrity basis for $\mathcal{P}^{\Gamma_\alpha}_{a_1}$ and $\{h_1, ..., h_l; j_1^{\Gamma_\beta}, ..., j^{\Gamma_\beta}_{p_{\Gamma_\beta}}\}$ an integrity basis for $\mathcal{P}^{\Gamma_\beta}_{a_2}$. $\{f_1, ..., f_k, h_1, ..., h_l\}$ will constitute a set of primary invariants for $\mathcal{P}^{[2]}$. The Clebsch-Gordan coefficients allow to construct $c^{\Gamma_f}_{\Gamma_\alpha,\Gamma_\beta}$ numerator polynomials of type $\Gamma_f, 1$ of $\mathcal{P}^{[2]}$ from each pair $(g_a^{\Gamma_\alpha}, j_b^{\Gamma_\beta})$, see Ref.[44] (Sect. 5.6). We write these functions $m^{\Gamma_f,1}_{\Gamma_\alpha,\Gamma_\beta,a,b,i}$, where $i \leq c^{\Gamma_f}_{\Gamma_\alpha,\Gamma_\beta}$. The integrity basis for ${\mathcal{P}^{[2]}}^{\Gamma_f,1}$ is then given by the denominator polynomials $\{f_1, ..., f_k, h_1, ..., h_l\}$ and the set of Γ_f–covariants numerator polynomials $\bigcup_{\Gamma_\alpha,\Gamma_\beta} \{m^{\Gamma_f,1}_{\Gamma_\alpha,\Gamma_\beta,a,b,i}, a \leq q_{a_1,\Gamma_\alpha}, b \leq q_{a_2,\Gamma_\beta}, i \leq c^{\Gamma_f}_{\Gamma_\alpha,\Gamma_\beta}\}$. As already mentionned, an integrity basis for ${\mathcal{P}^{[2]}}^{\Gamma_f}$ is easily generated from one of ${\mathcal{P}^{[2]}}^{\Gamma_f,1}$ see Ref.[44] (Sect. 3-18). The process is iterated by substituting ${\mathcal{P}^{[2]}}^{\Gamma_\alpha}$ to $\mathcal{P}^{\Gamma_\alpha}_{a_1}$ and $\mathcal{P}^{\Gamma_\beta}_{a_3}$ to $\mathcal{P}^{\Gamma_\beta}_{a_2}$, and so on recursively.

III. APPLICATION TO THE CONSTRUCTION OF INTEGRITY BASES FOR XY_4 MOLECULES

Our main goal is to generate in the most economical way, integrity bases for representations of symmetry groups on vector spaces spanned by molecular internal degrees of freedom. We focus, from now on, on the example of XY_4 molecules, but the following method holds in general.

We consider coordinates for the internal degrees of freedom adapted to the T_d symmetry point group of the molecule, which is isomorphous to the permutation group $\mathcal{S}_4$. For example, they can be the usual T_d–adapted coordinates used in many studies on XY_4 molecules[28], denoted by S_1, S_{2a}, S_{2b}, S_{3x}, S_{3y}, S_{3z}, S_{4x}, S_{4y}, and S_{4z}. S_1 transforms as the irreducible representation A_1, the pair S_{2a}, S_{2b} transforms as E, while both triplets S_{3x}, S_{3y}, S_{3z} and S_{4x}, S_{4y}, and S_{4z} transform as F_2. So, the representation of T_d on the vector space $\mathcal{Q} := \mathbb{R} < S_1, S_{2a}, ..., S_{4z} >$ generated by $S_1, S_{2a}, ..., S_{4z}$ splits into a direct sum of irreps.:

$$\mathcal{Q} = \mathbb{R} < S_1 > \oplus \mathbb{R} < S_{2a}, S_{2b} > \oplus \mathbb{R} < S_{3x}, S_{3y}, S_{3z} > \oplus \mathbb{R} < S_{4x}, S_{4y}, S_{4z} > . \quad (6)$$

An extra coordinate S_5 has to be added to map biunivoquely the whole nuclear configuration manifold, if the coordinates are $O(3)$-invariant (such as linear combinations of bond distances and bond angles, and no dihedral angle)[17]. In this case, polynomials involved in the computation of the PES, the DMS and other physically relevant quantities have to be expressed as $P = P_0 + P_1 S_5 + P_2 S_5^2 + P_3 S_5^3$, where the P_i are polynomials in the coordinates $S_1, S_{2a}, S_{2b}, S_{3x}, S_{3y}, S_{3z}, S_{4x}, S_{4y}, S_{4z}$.

However, since S_5 can be chosen to carry the A_1 representation, this extra-coordinate can be handled independently of the computation of Γ_f-covariants. The same remark applies to S_1: General Γ_f-covariants can be expressed as $P_0 R_0 + P_1 R_1 S_5 + P_2 R_2 S_5^2 + P_3 R_3 S_5^3$, where the R_i are arbitrary polynomials in S_1 and the P_i are Γ_f-covariant polynomials of $S_{2a}, S_{2b}, S_{3x}, S_{3y}, S_{3z}, S_{4x}, S_{4y}, S_{4z}$. This allows us to reduce the problem to the study of $\mathcal{P}^{\Gamma_f}$, where $\mathcal{P}$ is the polynomial algebra generated by $S_{2a}, S_{2b}, S_{3x}, S_{3y}, S_{3z}, S_{4x}, S_{4y}, S_{4z}$.

The octahedral group O and the group T_d both belong to the category of cubic point groups and share similar properties. Integrity bases related to the Molien generating functions $M(\Gamma_f; \Gamma_i; t)$ (Γ_i and Γ_f irreps.) are known for O, see[47] and Appendix. The denominator and numerator polynomials of these integrity basis will be the building blocks of the construction of the integrity basis for the initial reducible representation, $\mathcal{Q}' := \mathbb{R} < S_{2a}, S_{2b} > \oplus \mathbb{R} < S_{3x}, S_{3y}, S_{3z} > \oplus \mathbb{R} < S_{4x}, S_{4y}, S_{4z} >$ of the tetrahedral group T_d.

A. Denominator polynomials of the integrity bases

Denominator polynomials of the integrity basis of a reducible representation is just the union of the denominator polynomials of its irreducible subrepresentations. The form of the 8 denominator polynomials $f_2, ..., f_9$ (the shift in the indexing is motivated by the convention $f_1 := S_1$) for $\mathcal{Q}'$ is familiar[17]. they consist in two denominator polynomials of the module of T_d-invariant polynomials in S_{2a}, S_{2b}, $\mathbb{R}[S_{2a}, S_{2b}]^{\mathrm{T}_d}$, three denominator polynomials of $\mathbb{R}[S_{3x}, S_{3y}, S_{3z}]^{\mathrm{T}_d}$ and of three denominator polynomials of $\mathbb{R}[S_{4x}, S_{4y}, S_{4z}]^{\mathrm{T}_d}$. We list them below by degrees of increasing order:

1. Degree 2:

$$f_2 := \frac{S_{2a}^2 + S_{2b}^2}{\sqrt{2}} \tag{7}$$

$$f_3 := \frac{S_{3x}^2 + S_{3y}^2 + S_{3z}^2}{\sqrt{3}} \tag{8}$$

$$f_4 := \frac{S_{4x}^2 + S_{4y}^2 + S_{4z}^2}{\sqrt{3}} \tag{9}$$

2. Degree 3:

$$f_5 := \frac{-S_{2a}^3 + 3S_{2b}^2 S_{2a}}{2} \tag{10}$$

$$f_6 := S_{3x} S_{3y} S_{3z} \tag{11}$$

$$f_7 := S_{4x} S_{4y} S_{4z} \tag{12}$$

3. Degree 4:

$$f_8 := \frac{S_{3x}^4 + S_{3y}^4 + S_{3z}^4}{\sqrt{3}} \tag{13}$$

$$f_9 := \frac{S_{4x}^4 + S_{4y}^4 + S_{4z}^4}{\sqrt{3}} \ . \tag{14}$$

B. Numerator polynomials of the integrity bases

The Molien series for the action of T_d on $\mathcal{Q}'$ can be directly computed using Burnside's generalization[48] of the Molien's results[45]. However, it is computationally more efficient to use Eq. (5) to construct Molien generating functions and integrity bases. A non–zero $c_{\Gamma_\alpha, \Gamma_\beta}^{\Gamma_f}$ in the sum of Eq. (5) relates to a term in the numerator of $M^G\left(\Gamma_f; \mathcal{Q}_{a_1} \oplus ... \oplus \mathcal{Q}_{a_i}; t\right)$ and the corresponding polynomial is built by coupling previously obtained polynomials with Clebsch–Gordan coefficients of the group T_d.

As an example, using t_3 and t_4 to distinguish notationally the copies of t arising from the two Molien series in right hand side of Eq.(5),

$$\begin{aligned}
&M^{\mathrm{T}_d}\left(E; F_2 \oplus F_2; t_3, t_4\right) \\
&= M^{\mathrm{T}_d}\left(A_1; F_2; t_3\right) M^{\mathrm{T}_d}\left(E; F_2; t_4\right) \\
&\quad + M^{\mathrm{T}_d}\left(E; F_2; t_3\right) M^{\mathrm{T}_d}\left(A_1; F_2; t_4\right) \\
&\quad + M^{\mathrm{T}_d}\left(A_2; F_2; t_3\right) M^{\mathrm{T}_d}\left(E; F_2; t_4\right) \\
&\quad + M^{\mathrm{T}_d}\left(E; F_2; t_3\right) M^{\mathrm{T}_d}\left(A_2; F_2; t_4\right) \\
&\quad + M^{\mathrm{T}_d}\left(E; F_2; t_3\right) M^{\mathrm{T}_d}\left(E; F_2; t_4\right) \\
&\quad + M^{\mathrm{T}_d}\left(F_1; F_2; t_3\right) M^{\mathrm{T}_d}\left(F_1; F_2; t_4\right) \\
&\quad + M^{\mathrm{T}_d}\left(F_1; F_2; t_3\right) M^{\mathrm{T}_d}\left(F_2; F_2; t_4\right) \\
&\quad + M^{\mathrm{T}_d}\left(F_2; F_2; t_3\right) M^{\mathrm{T}_d}\left(F_1; F_2; t_4\right) \\
&\quad + M^{\mathrm{T}_d}\left(F_2; F_2; t_3\right) M^{\mathrm{T}_d}\left(F_2; F_2; t_4\right) \\
&= \frac{1}{\mathcal{D}\left(F_2; t_3\right) \mathcal{D}\left(F_2; t_4\right)} \left\{ t_4^2 + t_4^4 + t_3^2 + t_3^4 \right. \\
&\quad + t_3^6 t_4^2 + t_3^6 t_4^4 + t_3^2 t_4^6 + t_3^4 t_4^6 \\
&\quad + t_3^2 t_4^2 + t_3^2 t_4^4 + t_3^4 t_4^2 + t_3^4 t_4^4 \\
&\quad + t_3^3 t_4^3 + t_3^3 t_4^4 + t_3^4 t_4^3 + t_3^3 t_4^5 + t_3^4 t_4^4 + t_3^5 t_4^3 + t_3^4 t_4^5 + t_3^5 t_4^4 + t_3^5 t_4^5 \\
&\quad + t_3^3 t_4 + t_3^3 t_4^2 + t_3^4 t_4 + t_3^3 t_4^3 + t_3^4 t_4^2 + t_3^5 t_4 + t_3^4 t_4^3 + t_3^5 t_4^2 + t_3^5 t_4^3 \\
&\quad + t_3 t_4^3 + t_3 t_4^4 + t_3^2 t_4^3 + t_3 t_4^5 + t_3^2 t_4^4 + t_3^3 t_4^3 + t_3^2 t_4^5 + t_3^3 t_4^4 + t_3^3 t_4^5 \\
&\quad \left. + t_3 t_4 + t_3 t_4^2 + t_3^2 t_4 + t_3 t_4^3 + t_3^2 t_4^2 + t_3^3 t_4 + t_3^2 t_4^3 + t_3^3 t_4^2 + t_3^3 t_4^3 \right\}
\end{aligned}$$

with

$$\mathcal{D}\left(F_2; t\right) = \left(1 - t^2\right)\left(1 - t^3\right)\left(1 - t^4\right).$$

In total, the number of $E, 1$–covariant basis polynomials for the initial representation $F_2 \oplus F_2$ is 48. More precisely, the first two lines of the first equality lead to the first line of the second equality which says that two of the required $E, 1$–covariant basis polynomials associated to the numerator of $M^{\mathrm{T}_d}\left(E; F_2 \oplus F_2\right)$ are built by coupling through Clebsch–Gordan coefficients the numerator polynomial of degree zero in the integrity basis associated to $M^{\mathrm{T}_d}\left(A_1; F_2; t_3\right)$ with the numerator polynomials of degree two and four in the integrity basis associated to $M^{\mathrm{T}_d}\left(E; F_2; t_4\right)$ and two others are obtained by reversing the part of $M^{\mathrm{T}_d}\left(A_1; F_2; t_3\right)$ and $M^{\mathrm{T}_d}\left(E; F_2; t_4\right)$. Similarly, the 4 terms of the second line of the second equality correspond to the 4 E–covariant numerator polynomials arising from the product A_2 and E numerator polynomials of the integrity basis of the F_2 irreducible representation. The following lines of the second equality gather the contributions of the succesive lines of the first equality, respecting their order.

This method has the advantage that only the integrity bases for initial irreps., see Appendix, and the Clebsch–Gordan are required. In practice we couple first the two symmetrized F_2 coordinates S_{3x}, S_{3y}, S_{3z} and S_{4x}, S_{4y}, S_{4z}. We then couple the results with the coordinates S_{2a} and S_{2b}, and finally with the coordinate S_1.

The fully coupled generating function for the F_2 final irreducible representation reads:

$$M^{\mathrm{T}_d}\left(F_2;\mathcal{Q}';t\right)=\frac{\mathcal{N}\left(F_2;\mathcal{Q}';t\right)}{(1-t^2)^3(1-t^3)^3(1-t^4)^2},\qquad(15)$$

with

$$\begin{aligned}&\mathcal{N}\left(F_2;\mathcal{Q}';t\right)\\&=\;2t+5t^2+12t^3+23t^4+41t^5+60t^6+71t^7+71t^8\\&\quad+60t^9+45t^{10}+27t^{11}+12t^{12}+3t^{13}.\end{aligned}$$

The Molien series numerator coefficients for all irreps. are given in Table I.

As far as the F_2 representation is concerned, there are 432 F_2-covariants of type "z" (we use this notation instead of "1" used in the section II because it refers to the usual basis set labelling for F_2-representation in a geometrical context), $g_1^{F_2,z},...,g_{432}^{F_2,z}$ of which 2 are of degree one, 5 of degree two, 12 of degree three, and so on. We finally obtain that an arbitrary F_2–covariant of type $m\in\{x,y,z\}$ in the algebra spanned by the $S_1,\ldots,S_{4z}$ coordinates will identify with a unique linear combination of monomials:

$$f_1^{j_1}f_2^{j_2}...f_9^{j_9}g_k^{F_2,m}\quad(j_1,\ldots j_9)\in\mathbb{N}^9,\;1\leq k\leq 432.\qquad(16)$$

Lists of numerator polynomials for all irreps. and all types are provided as supplementary material[41]. They have been derived in a few seconds of CPU time on a laptop by using the symbolic algebra code MAPLE[49].

The knowledge of the polynomials in our integrity bases is sufficient to generate all the polynomials up to any degree, only multiplications between denominator polynomials and one numerator polynomial are necessary. The gain with respect to classical methods of group theory already shows up at degree 4: we only need the 9 basic invariants and the 16 A_1-covariants (i.e. secondary invariants) up to degree 4, to generate all 33 linearly independent invariants of degree 4 for representation $\mathcal{Q}$, see Tab.I and compare with Ref.[7]. In this article, only a 6-dimensional representation is considered (the S_{3x},S_{3y},S_{3z} coordinates are left out). In fact, an integrity basis of 6 basic invariants and 3 secondary invariants can generate 11 linearly independent A_1–invariants of degree 4, which will span the same vector space as those tabulated in the last table of Ref.[7]. Similar remarks apply to the covariants. The gain becomes rapidly more spectacular as the degree increases. PES of order 10 have already been calculated for methane[15,32]. There are 1998 linearly independent invariants of degree 10 for representation $\mathcal{Q}$. They can be generated with only the 9 basic invariants and 132 secondary invariants. Similarly, EDMS for methane of order 6 have already appeared in the literature[37,50]. The 9 basic invariants and 143 F_2,z-covariant numerator polynomials of degree less or equal to 6 (see Tab.I) are enough to generate the 400 linearly independent polynomials required to span the vector space of F_2,z-covariant polynomials of sixth degree.

IV. CONCLUSION

We have determined for the first time integrity bases of the Γ_f–covariants of the group T_d acting on the symmetrized internal coordinates of a XY_4 molecule. They are composed of nine algebraically independent denominator polynomials and a finite number of Γ_f–covariant numerator polynomials given in supplementary material[41]. We have taken advantage of symmetry–adapted internal coordinates spanning the reducible representation $A_1\oplus E\oplus F_2\oplus F_2$ of T_d to construct an integrity basis for each final representation Γ_f. Integrity basis sets are first determined for each single, possibly degenerate, irreducible representation of the group. These integrity bases are coupled successively in a second step by using the Clebsch–Gordan coefficients of the group T_d. This strategy to derive the Γ_f–covariants is general since the Γ_f–covariant polynomials admit a Hironaka decomposition[43] for any finite group G. In fact, our approach makes available for the study of global PES and other functions of nuclear geometric configurations the recent tools of ring and invariant theory such as Cohen–Macaulay–type properties and the effective computational tools of modern commutative algebra[38], which go far beyond the classical Molien series approach in quantum chemistry. Finally, our method based on integrity bases is more efficient than classical methods of group theory based on the construction degree by degree of the symmetry–adapted terms to be included in the potential energy surface or the electric dipole moment surface. All the required polynomials up to any order are generated by simple multiplications between polynomials in the integrity bases of this paper.

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Appendix: Generating functions and corresponding integrity bases for irreducible representations of T_d

The T_d point group has five irreps.: A_1, A_2, E, F_1 and F_2. The irreducible representation E is doubly degenerate, while the F_1 and F_2 irreps. are triply degenerate.

The procedure detailed in the main text is based on the knowledge of the generating functions $M^{\mathrm{T}_d}\left(\Gamma_f;\Gamma_i;t\right)$, where Γ_i and Γ_f are irreps. of the group T_d. The coefficient c_n in the Taylor expansion $c_0+c_1t+c_2t^2+\cdots$ of the generating function gives the number of linearly independent Γ_f–covariant polynomials of degree n that

TABLE I: Numbers $n_k^{\Gamma_f}$ of Γ_f–covariant numerator polynomials of degree k and dimensions $\dim \mathcal{P}_k^{\Gamma_f,i}$, $1 \le i \le [\Gamma_f]$, of the vector spaces of Γ_f, i–covariants numerator polynomials of degree k, $\Gamma_f \in \{A_1, A_2, E, F_1, F_2\}$. The total number $\sum_{k=0}^{15} n_k^{\Gamma_f}$ of Γ_f–covariant numerator polynomials is equal to $[\Gamma_f] \times \Pi_j d_j/|G|$, where $[\Gamma_f]$ is the dimension of the irreducible representation Γ_f, $|G| = 24$ is the order of the group T_d, and $\Pi_j d_j = 3456$ is the product of the degrees of the nine denominator polynomials. This result is a generalized version of proposition 2.3.6 of Ref.[24]. It suffices to multiply the left–hand side of Eq. (2.3.4) by the complex conjugate of the character of π and to notice that this equals to $[\Gamma_f]$ for $\pi = Id$, see also Proposition 4.9 of Ref.[43].

Γ_f:	A_1		A_2		E		F_1		F_2	
Degree k	$n_k^{A_1}$	$\dim \mathcal{P}_k^{A_1}$	$n_k^{A_2}$	$\dim \mathcal{P}_k^{A_2}$	n_k^{E}	$\dim \mathcal{P}_k^{E,i}$	$n_k^{F_1}$	$\dim \mathcal{P}_k^{F_1,i}$	$n_k^{F_2}$	$\dim \mathcal{P}_k^{F_2,i}$
0	1	1	0	0	0	0	0	0	0	0
1	0	1	0	0	1	1	0	0	2	2
2	1	5	0	0	4	5	3	3	5	7
3	5	13	4	4	6	14	12	15	12	25
4	9	33	8	12	16	45	27	51	23	69
5	12	72	15	39	28	111	45	141	41	177
6	18	162	26	101	39	257	60	342	60	400
7	21	319	24	226	50	545	71	752	71	848
8	24	620	21	470	50	1090	71	1528	71	1672
9	26	1132	18	918	39	2040	60	2920	60	3140
10	15	1998	12	1680	28	3678	41	5298	45	5610
11	8	3384	9	2946	16	6330	23	9210	27	9654
12	4	5587	5	4973	6	10545	12	15418	12	16022
13	0	8912	1	8098	4	17010	5	24998	3	25822
14	0	13912	0	12818	1	26730	2	39388	0	40472
15	0	21185	1	19771	0	40935	0	60536	0	61960
$n > 15$	0		0		0		0		0	0
Total	144	∞	144	∞	288	∞	432	∞	432	∞

can be constructed from the objects in the initial Γ_i representation.

Each generating function $M^{\mathrm{T}_d}(\Gamma_f;\Gamma_i;t)$ is the ratio of a numerator $\mathcal{N}(\Gamma_f;\Gamma_i;t)$ over a denominator $\mathcal{D}(\Gamma_i;t)$:

$$M^{\mathrm{T}_d}(\Gamma_f;\Gamma_i;t)=\frac{\mathcal{N}(\Gamma_f;\Gamma_i;t)}{\mathcal{D}(\Gamma_i;t)}=\frac{\sum\limits_{k=1}^{N} t^{\nu_k}}{\prod\limits_{k=1}^{D}\left(1-t^{\delta_k}\right)}, \quad \text{(A.1)}$$

with $\nu_k \in \mathbb{N}$ and $\delta_k \in \mathbb{N}\backslash\{0\}$. The polynomial associated to a $\left(1-t^{\delta_k}\right)$ term in the denominator is an invariant called a denominator polynomial of degree δ_k and is noted $I^{(\delta_k)}(\Gamma_i)$. The polynomial associated to a t^{ν_k} term in the numerator is a Γ_f–covariant called a numerator polynomial of degree ν_k and is noted $E^{(\nu_k)}(\Gamma_f;\Gamma_i)$ (when Γ_f is degenerate, $E^{(\nu_k)}(\Gamma_f;\Gamma_i)$ will be a vector gathering all the Γ_f,i–covariant numerator polynomials of degree ν_k for $i\in\{1,[\Gamma_f]\}$). Inspection of A.1 indicates that D denominator polynomials and N numerator polynomials are associated to the generating function $M^{\mathrm{T}_d}(\Gamma_f;\Gamma_i;t)$.

The notation for denominator and numerator polynomials using α,β,γ symbols for a chosen basis of the irreps. closely follows the paper of Patera, Sharp and Winternitz[47]. However, their table for octahedral tensors contains two errors for the degree eight $E^{(8)}(\Gamma_4,\Gamma_4)$ and degree seven $E^{(7)}(\Gamma_5,\Gamma_4)$ numerator polynomials. With the definitions of polynomials given in paper[47], the following relation hold:

$$\begin{aligned}E^{(8)}(\Gamma_4,\Gamma_4)_i &= I^{(2)}(\Gamma_4)E^{(6)}(\Gamma_4,\Gamma_4)_i\\ &-\frac{1}{2}I^{(2)}(\Gamma_4)^2E^{(4)}(\Gamma_4,\Gamma_4)_i\\ &+\frac{1}{2}I^{(4)}(\Gamma_4)E^{(4)}(\Gamma_4,\Gamma_4)_i\,, \quad \text{(A.2)}\end{aligned}$$

where the index i stands either for x, y or z. The relation (A.2) indicates that the polynomial of degree eight $E^{(8)}(\Gamma_4,\Gamma_4)$ has a decomposition in terms of polynomials that are elements of the integrity basis of $M^{\mathrm{T}_d}(\Gamma_4;\Gamma_4;t)$. As a consequence, $E^{(8)}(\Gamma_4,\Gamma_4)$ does not enter the integrity basis.

The same is true for $E^{(7)}(\Gamma_5,\Gamma_4)$ and the integrity basis of $M^{\mathrm{T}_d}(\Gamma_5;\Gamma_4;t)$ due to relation (A.3).

$$\begin{aligned}E^{(7)}(\Gamma_5,\Gamma_4)_i &= I^{(2)}(\Gamma_4)E^{(5)}(\Gamma_5,\Gamma_4)_i\\ &-\frac{1}{2}I^{(2)}(\Gamma_4)^2E^{(3)}(\Gamma_5,\Gamma_4)_i\\ &+\frac{1}{2}I^{(4)}(\Gamma_4)E^{(3)}(\Gamma_5,\Gamma_4)_i\,. \quad \text{(A.3)}\end{aligned}$$

A complete list of tables of both denominator and numerator polynomials for all the initial Γ_i and final Γ_f irreps. is given in the next sections.

1. $\Gamma_i = A_1$ irreducible representation

The denominator is $\mathcal{D}(A_1;t)=1-t$. The corresponding denominator polynomial of degree one is $I^{(1)}(A_1)=\alpha$. The only non–zero numerator polynomial is $\mathcal{N}(A_1;A_1;t)=1$.

2. $\Gamma_i = A_2$ irreducible representation

The denominator is $\mathcal{D}(A_2;t)=1-t^2$. The corresponding denominator polynomial of degree two is $I^{(2)}(A_2)=\alpha^2$. Two numerator polynomials are non–zero: $\mathcal{N}(A_1;A_2;t)=1$ and $\mathcal{N}(A_2;A_2;t)=t$. The A_2–covariant numerator polynomial of degree one is

$$E^{(1)}(A_2;A_2)=\alpha.$$

3. $\Gamma_i = E$ irreducible representation

The denominator is $\mathcal{D}(E;t)=\left(1-t^2\right)\left(1-t^3\right)$. The denominator polynomial of degree two is $I^{(2)}(E)=\frac{\alpha^2+\beta^2}{\sqrt{2}}$ and the denominator polynomial of degree three is $I^{(3)}(E)=\frac{-\alpha^3+3\alpha\beta^2}{2}$. Three numerator polynomials are non–zero: $\mathcal{N}(A_1;E;t)=1$, $\mathcal{N}(A_2;E;t)=t^3$, and $\mathcal{N}(E;E;t)=t+t^2$. The A_2–covariant numerator polynomial of degree three is

$$E^{(3)}(A_2;E)=\frac{-3\alpha^2\beta+\beta^3}{2},$$

and the two E–covariant numerator polynomials of degree one and two are

$$\begin{aligned}E^{(1)}(E;E) &= \begin{pmatrix}\alpha\\ \beta\end{pmatrix}\\ E^{(2)}(E;E) &= \frac{1}{\sqrt{2}}\begin{pmatrix}-\alpha^2+\beta^2\\ 2\alpha\beta\end{pmatrix}\end{aligned}$$

4. $\Gamma_i = F_1$ irreducible representation

The denominator is $\mathcal{D}(F_1;t)=\left(1-t^2\right)\left(1-t^4\right)\left(1-t^6\right)$. The denominator polynomial of degree two is $I^{(2)}(F_1)=\frac{\alpha^2+\beta^2+\gamma^2}{\sqrt{3}}$, the denominator polynomial of degree four is $I^{(4)}(F_1)=\frac{\alpha^4+\beta^4+\gamma^4}{\sqrt{3}}$ and the denominator polynomial of degree six is $I^{(6)}(F_1)=\frac{\alpha^6+\beta^6+\gamma^6}{\sqrt{3}}$. The numerator polynomials are $\mathcal{N}(A_1;F_1;t)=1+t^9$, $\mathcal{N}(A_2;F_1;t)=t^3+t^6$ $\mathcal{N}(E;F_1;t)=t^2+t^4+t^5+t^7$ $\mathcal{N}(F_1;F_1;t)=t+t^3+t^4+t^5+t^6+t^8$, and $\mathcal{N}(F_2;F_1;t)=t^2+t^3+t^4+t^5+t^6+t^7$. The invariant numerator polynomial of degree nine is

$$E^{(9)}(A_1;F_1)=\frac{1}{\sqrt{6}}\alpha\beta\gamma\left(\alpha^2-\beta^2\right)\left(\beta^2-\gamma^2\right)\left(\gamma^2-\alpha^2\right),$$

the two A_2–covariant numerator polynomials of degree three and six are

$$E^{(3)}(A_2;F_1) = \alpha\beta\gamma$$
$$E^{(6)}(A_2;F_1) = \frac{1}{\sqrt{6}}\left(\alpha^2-\beta^2\right)\left(\beta^2-\gamma^2\right)\left(\gamma^2-\alpha^2\right),$$

the four E–covariant numerator polynomials of degree two, four, five, and seven are:

$$E^{(2)}(E;F_1) = \frac{1}{\sqrt{6}}\begin{pmatrix}\alpha^2+\beta^2-2\gamma^2\\ \sqrt{3}\left(-\alpha^2+\beta^2\right)\end{pmatrix}$$
$$E^{(4)}(E;F_1) = \frac{1}{\sqrt{6}}\begin{pmatrix}\alpha^4+\beta^4-2\gamma^4\\ \sqrt{3}\left(-\alpha^4+\beta^4\right)\end{pmatrix}$$
$$E^{(5)}(E;F_1) = \frac{1}{\sqrt{6}}\alpha\beta\gamma\begin{pmatrix}\sqrt{3}\left(\alpha^2-\beta^2\right)\\ \alpha^2+\beta^2-2\gamma^2\end{pmatrix}$$
$$E^{(7)}(E;F_1) = \frac{1}{\sqrt{6}}\alpha\beta\gamma\begin{pmatrix}\sqrt{3}\left(\alpha^4-\beta^4\right)\\ \alpha^4+\beta^4-2\gamma^4\end{pmatrix},$$

the six F_1–covariant numerator polynomials of degree one, three, four, five, six, and eight are

$$E^{(1)}(F_1;F_1) = \begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix}$$
$$E^{(3)}(F_1;F_1) = \begin{pmatrix}\alpha^3\\ \beta^3\\ \gamma^3\end{pmatrix}$$
$$E^{(4)}(F_1;F_1) = \frac{1}{\sqrt{2}}\begin{pmatrix}\left(\beta^2-\gamma^2\right)\beta\gamma\\ \left(\gamma^2-\alpha^2\right)\gamma\alpha\\ \left(\alpha^2-\beta^2\right)\alpha\beta\end{pmatrix}$$
$$E^{(5)}(F_1;F_1) = \begin{pmatrix}\alpha^5\\ \beta^5\\ \gamma^5\end{pmatrix}$$
$$E^{(6)}(F_1;F_1) = \frac{1}{\sqrt{2}}\begin{pmatrix}\left(\beta^4-\gamma^4\right)\beta\gamma\\ \left(\gamma^4-\alpha^4\right)\gamma\alpha\\ \left(\alpha^4-\beta^4\right)\alpha\beta\end{pmatrix}$$
$$E^{(8)}(F_1;F_1) = \frac{1}{\sqrt{2}}\alpha\beta\gamma\begin{pmatrix}\left(\beta^4-\gamma^4\right)\alpha\\ \left(\gamma^4-\alpha^4\right)\beta\\ \left(\alpha^4-\beta^4\right)\gamma\end{pmatrix},$$

the six F_2–covariant numerator polynomials of degree two, three, four, five, six, and seven are

$$E^{(2)}(F_2;F_1) = \begin{pmatrix}\beta\gamma\\ \gamma\alpha\\ \alpha\beta\end{pmatrix}$$
$$E^{(3)}(F_2;F_1) = \frac{1}{\sqrt{2}}\begin{pmatrix}\left(\beta^2-\gamma^2\right)\alpha\\ \left(\gamma^2-\alpha^2\right)\beta\\ \left(\alpha^2-\beta^2\right)\gamma\end{pmatrix}$$
$$E^{(4)}(F_2;F_1) = \alpha\beta\gamma\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix}$$
$$E^{(5)}(F_2;F_1) = \frac{1}{\sqrt{2}}\begin{pmatrix}\left(\beta^4-\gamma^4\right)\alpha\\ \left(\gamma^4-\alpha^4\right)\beta\\ \left(\alpha^4-\beta^4\right)\gamma\end{pmatrix}$$
$$E^{(6)}(F_2;F_1) = \alpha\beta\gamma\begin{pmatrix}\alpha^3\\ \beta^3\\ \gamma^3\end{pmatrix}$$
$$E^{(7)}(F_2;F_1) = \frac{1}{\sqrt{2}}\alpha\beta\gamma\begin{pmatrix}\left(\beta^2-\gamma^2\right)\beta\gamma\\ \left(\gamma^2-\alpha^2\right)\alpha\gamma\\ \left(\alpha^2-\beta^2\right)\alpha\beta\end{pmatrix}$$

5. $\Gamma_i = F_2$ irreducible representation

The denominator is $\mathcal{D}(F_2;t) = \left(1-t^2\right)\left(1-t^3\right)\left(1-t^4\right)$. The denominator polynomial of degree two is $I^{(2)}(F_2) = \frac{\alpha^2+\beta^2+\gamma^2}{\sqrt{3}}$, the denominator polynomial of degree three is $I^{(3)}(F_2) = \alpha\beta\gamma$ and the denominator polynomial of degree four is $I^{(4)}(F_2) = \frac{\alpha^4+\beta^4+\gamma^4}{\sqrt{3}}$. The numerator polynomials are $\mathcal{N}(A_1;F_2;t) = 1$, $\mathcal{N}(A_2;F_2;t) = t^6$, $\mathcal{N}(E;F_2;t) = t^2+t^4$, $\mathcal{N}(F_1;F_2;t) = t^3+t^4+t^5$, and $\mathcal{N}(F_2;F_2;t) = t+t^2+t^3$. The A_2–covariant numerator polynomial of degree six is

$$E^{(6)}(A_2;F_2) = \frac{1}{\sqrt{6}}\left(\alpha^2-\beta^2\right)\left(\beta^2-\gamma^2\right)\left(\gamma^2-\alpha^2\right),$$

the two E–covariant numerator polynomials of degree two and four are

$$E^{(2)}(E;F_2) = \frac{1}{\sqrt{6}}\begin{pmatrix}\alpha^2+\beta^2-2\gamma^2\\ \sqrt{3}\left(-\alpha^2+\beta^2\right)\end{pmatrix}$$
$$E^{(4)}(E;F_2) = \frac{1}{\sqrt{6}}\begin{pmatrix}\alpha^4+\beta^4-2\gamma^4\\ \sqrt{3}\left(-\alpha^4+\beta^4\right)\end{pmatrix},$$

the four F_1–covariant numerator polynomials of degree three, four and five are

$$E^{(3)}(F_1;F_2) = \frac{1}{\sqrt{2}}\begin{pmatrix}\left(\beta^2-\gamma^2\right)\alpha\\ \left(\gamma^2-\alpha^2\right)\beta\\ \left(\alpha^2-\beta^2\right)\gamma\end{pmatrix}$$
$$E^{(4)}(F_1;F_2) = \frac{1}{\sqrt{2}}\begin{pmatrix}\left(\beta^2-\gamma^2\right)\beta\gamma\\ \left(\gamma^2-\alpha^2\right)\gamma\alpha\\ \left(\alpha^2-\beta^2\right)\alpha\beta\end{pmatrix}$$
$$E^{(5)}(F_1;F_2) = \frac{1}{\sqrt{2}}\begin{pmatrix}\left(\beta^2-\gamma^2\right)\alpha^3\\ \left(\gamma^2-\alpha^2\right)\beta^3\\ \left(\alpha^2-\beta^2\right)\gamma^3\end{pmatrix},$$

the three F_2–covariant numerator polynomials of degree one, two, and three are

$$E^{(1)}\left(F_2;F_2\right) = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$
$$E^{(2)}\left(F_2;F_2\right) = \begin{pmatrix} \beta\gamma \\ \gamma\alpha \\ \alpha\beta \end{pmatrix}$$
$$E^{(3)}\left(F_2;F_2\right) = \begin{pmatrix} \alpha^3 \\ \beta^3 \\ \gamma^3 \end{pmatrix}.$$

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