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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<sup>1–5</sup> 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  $\Gamma_i$ . Symmetry-adapted polynomials in these variables are then considered. The polynomials that transform according to the final irreducible representation  $\Gamma_f$  are called  $\Gamma_f$ -covariant polynomials.<sup>6</sup> A  $\Gamma_f$ -covariant polynomial is called an invariant polynomial

if the  $\Gamma_f$  representation is the trivial representation of the group.

The projector or Reynolds operator is a standard method of group theory to generate invariant and  $\Gamma_f$ -covariant polynomials. Marquardt<sup>7</sup> and Schwenke<sup>8</sup> 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,<sup>9</sup> Bunker,<sup>4</sup> Lomont,<sup>10</sup> and Taylor.<sup>11</sup> 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 latter 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  $\Gamma_f$ -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.<sup>12–15</sup> 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<sup>16,17</sup> 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.*<sup>18,19</sup>. Followers include Collins and Parsons,<sup>20</sup> Ischtwan and Peyerimhoff,<sup>21</sup> and, more recently, Braams and Bowman.<sup>22</sup> 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  $\Gamma_f$ -covariant polynomials is a finite set of polynomials with the special property that any  $\Gamma_f$ -covariant uniquely decomposes as a polynomial function in the elements of the integrity basis. The integrity basis contains two partitions.<sup>16,23</sup> The first partition contains the so-called denominator or primary polynomials.<sup>16,24</sup> They are invariant polynomials and their corresponding power in the decomposition of a  $\Gamma_f$ -covariant can be any natural integer. The second subset contains the numerator or secondary polynomials. They transform as the  $\Gamma_f$  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<sup>17</sup> 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  $O(3)$ .<sup>23,25,26</sup> 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.<sup>23,27</sup>

The focus of the present article is on the  $\Gamma_f$ -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),<sup>28,29</sup> Cartesian normal coordinates,<sup>28,30-34</sup> symmetrized coordinates based on Morse coordinates on Radau vectors for stretching modes and cosines of valence bond angles for bending modes,<sup>8</sup> haversines of bond angles,<sup>35</sup> cosines of valence bond angles times functions of bond lengths,<sup>36</sup> symmetrized coordinates based on bond lengths, interbond angles and torsion angles,<sup>15</sup> or interbond angles and bond lengths times a gaussian exponential factor.<sup>37</sup>

The purpose of the present article is to show on the explicit example of a  $XY_4$  molecule that the techniques of invariant theory that were used to obtain a polynomial basis set for totally symmetrical quantities<sup>17</sup> are straightforwardly extended to quantities transforming according to an arbitrary irreducible representation  $\Gamma_f$  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.<sup>38</sup>). However, on the one hand, existing methods of computational invariant theory<sup>24,39,40</sup> 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  $\Gamma_f$ -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<sup>41</sup>. 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 developed, both in mathematics and in chemical physics. Classical references on the subject in mathematics are the books by Benson<sup>42</sup> and Stanley<sup>43</sup>. Schmelzer and Murrell<sup>19</sup> have had a pioneering influence as far as the construction of a PES is concerned. Refs.<sup>16,44</sup> 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.<sup>43</sup> 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,  $Q_1, \dots, Q_k$ , 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  $\mathcal{Q} = \langle Q_1, \dots, Q_k \rangle$  spanned by  $Q_1, \dots, Q_k$ . This action extends naturally to  $\mathcal{P}$ .

Let  $\mathcal{P}^{\Gamma_f}$  be the vector subspace of polynomials transforming as the irreducible representation  $\Gamma_f$ . We write  $[\Gamma_f]$  for the dimension of  $\Gamma_f$ . 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  $\Gamma_f$ -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  $\Gamma_f$  has a distinguished basis  $\psi_1, \dots, \psi_{[\Gamma_f]}$ . The polynomials  $P$  in  $\mathcal{P}^{\Gamma_f}$  can then be decomposed further as a sum of polynomials,

$$P = \sum_{i=1}^{[\Gamma_f]} P_i, \quad (1)$$

each term behaving as a base function  $\psi_i$ , see e.g. Ref.<sup>44</sup> (Chap. 3). We will say that  $P_i$  is of type  $\Gamma_f, i$  and write

$\mathcal{P}^{\Gamma_f} = \bigoplus_{i=1}^{[\Gamma_f]} \mathcal{P}^{\Gamma_f, i}$  the corresponding decomposition of the vector space of  $\Gamma_f$ -covariant polynomials.

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

$$\mathcal{P}^{\Gamma_f} = \mathbb{C}[f_1, \dots, f_k] g_1^{\Gamma_f} \oplus \dots \oplus \mathbb{C}[f_1, \dots, f_k] g_{p_{\Gamma_f}}^{\Gamma_f}, \quad (2)$$

where  $\mathbb{C}[f_1, \dots, f_k]$  is the algebra spanned by the  $f_1, \dots, f_k$  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  $\Gamma_f$  is the trivial representation (so that  $\Gamma_f$ -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  $\Gamma_f$ -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  $\Gamma_f$ -covariant basis polynomials can be chosen as behaving as the basis functions  $\psi_i$  under the action of  $G$ . For each  $i$ ,  $1 \leq i \leq [\Gamma_f]$ , there are  $q_{\Gamma_f} = \frac{p_{\Gamma_f}}{[\Gamma_f]}$   $\Gamma_f$ -covariant basis polynomials of type  $i$ . Let us assume that the first  $q_{\Gamma_f}$   $\Gamma_f$ -covariant basis polynomials are of type 1:  $g_1^{\Gamma_f, 1}, \dots, g_{q_{\Gamma_f}}^{\Gamma_f, 1}$ . We will then refer to the whole set  $\{f_1, \dots, f_k; g_1^{\Gamma_f, 1}, \dots, g_{q_{\Gamma_f}}^{\Gamma_f, 1}\}$  as an integrity basis of the module  $\mathcal{P}^{\Gamma_f, 1}$  and to the particular set,  $g_1^{\Gamma_f, 1}, \dots, g_{q_{\Gamma_f}}^{\Gamma_f, 1}$ , as the set of  $\Gamma_f$ -covariant basis polynomials of type 1. Once these polynomials have been constructed, universal formulas allow to construct partner families of  $\Gamma_f$ -covariant polynomials of arbitrary type  $i > 1$ , see e.g. Ref.<sup>44</sup> (Sect. 3-18).

The elements of an integrity basis can always be chosen 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  $\Gamma_f$ -covariant basis polynomials and their degrees are fixed and determined by the so-called Molien series<sup>45</sup>.

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

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

where the second equality holds for all  $i \in \{1, \dots, [\Gamma_f]\}$ , 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  $\Gamma_f, i$  polynomials of degree  $n$ .

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

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

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  $\Gamma_f, i$ -covariant numerator polynomials of each degree is given by the corresponding coefficient of the polynomial  $M^G(\Gamma_f; \mathcal{Q}; t) \cdot (1 - t^{\deg(f_1)}) \dots (1 - t^{\deg(f_k)})$ . The problem of generating  $\mathcal{P}^{\Gamma_f, i}$  comes down to the computation of a complete set of such  $\Gamma_f, i$ -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,  $\mathcal{Q} = \mathcal{Q}_{a_1} \oplus \dots \oplus \mathcal{Q}_{a_n}$ . 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  $i^{\text{th}}$ -component,  $\mathcal{Q}^{[i]} := \mathcal{Q}_{a_1} \oplus \dots \oplus \mathcal{Q}_{a_i}$ , is written  $\mathcal{P}^{[i]}$ . We write  $M^G(\Gamma_f; \mathcal{Q}^{[i]}; t)$  for the Molien series associated to  $\Gamma_f$ -covariants on  $\mathcal{P}^{[i]}$ .

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

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

where the sum runs over all irreps  $\Gamma_\alpha$  and  $\Gamma_\beta$ . In case of the  $T_d$  point group,  $c_{\Gamma_\alpha, \Gamma_\beta}^{\Gamma_f} = 0$  or 1, see Ref.<sup>1</sup>.

The same recursion principle can be used to construct an integrity basis for  $\mathcal{P}^{\Gamma_f}$ . Let  $\{f_1, \dots, f_k; g_1^{\Gamma_\alpha}, \dots, g_{p_{\Gamma_\alpha}}^{\Gamma_\alpha}\}$  be an integrity basis for  $\mathcal{P}_{a_1}^{\Gamma_\alpha}$  and  $\{h_1, \dots, h_l; j_1^{\Gamma_\beta}, \dots, j_{p_{\Gamma_\beta}}^{\Gamma_\beta}\}$  an integrity basis for  $\mathcal{P}_{a_2}^{\Gamma_\beta}$ .  $\{f_1, \dots, f_k, h_1, \dots, h_l\}$  will constitute a set of primary invariants for  $\mathcal{P}^{[2]}$ . The Clebsch-Gordan coefficients allow to construct  $c_{\Gamma_\alpha, \Gamma_\beta}^{\Gamma_f}$  numerator polynomials of type  $\Gamma_f, 1$  of  $\mathcal{P}^{[2]}$  from each pair  $(g_a^{\Gamma_\alpha}, j_b^{\Gamma_\beta})$ , see Ref.<sup>44</sup> (Sect. 5.6). We write these functions  $m_{\Gamma_\alpha, \Gamma_\beta, a, b, i}^{\Gamma_f, 1}$ , where  $i \leq c_{\Gamma_\alpha, \Gamma_\beta}^{\Gamma_f}$ . The integrity basis for  $\mathcal{P}^{[2]\Gamma_f, 1}$  is then given by the denominator polynomials  $\{f_1, \dots, f_k, h_1, \dots, h_l\}$  and the set of  $\Gamma_f$ -covariants numerator polynomials  $\bigcup_{\Gamma_\alpha, \Gamma_\beta} \{m_{\Gamma_\alpha, \Gamma_\beta, a, b, i}^{\Gamma_f, 1}, a \leq q_{a_1, \Gamma_\alpha}, b \leq q_{a_2, \Gamma_\beta}, i \leq c_{\Gamma_\alpha, \Gamma_\beta}^{\Gamma_f}\}$ . As already mentioned, an integrity basis for  $\mathcal{P}^{[2]\Gamma_f}$  is easily generated from one of  $\mathcal{P}^{[2]\Gamma_f, 1}$  see Ref.<sup>44</sup> (Sect. 3-18). The process is iterated by substituting  $\mathcal{P}^{[2]\Gamma_\alpha}$  to  $\mathcal{P}_{a_1}^{\Gamma_\alpha}$  and  $\mathcal{P}_{a_3}^{\Gamma_\beta}$  to  $\mathcal{P}_{a_2}^{\Gamma_\beta}$ , 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  $S_4$ . For example, they can be the usual  $T_d$ -adapted coordinates used in many studies on  $XY_4$  molecules<sup>28</sup>, 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  $\mathcal{Q} := \mathbb{R} \langle S_1, S_{2a}, \dots, S_{4z} \rangle$  generated by  $S_1, S_{2a}, \dots, S_{4z}$  splits into a direct sum of irreps.:

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

An extra coordinate  $S_5$  has to be added to map bi-uniquely 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)<sup>17</sup>. 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  $\Gamma_f$ -covariants. The same remark applies to  $S_1$ : General  $\Gamma_f$ -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  $\Gamma_f$ -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  $M(\Gamma_f; \Gamma_i; t)$  ( $\Gamma_i$  and  $\Gamma_f$  irreps.) are known for  $O$ , see<sup>47</sup> 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,  $\mathcal{Q}' := \mathbb{R} \langle S_{2a}, S_{2b} \rangle \oplus \mathbb{R} \langle S_{3x}, S_{3y}, S_{3z} \rangle \oplus \mathbb{R} \langle S_{4x}, S_{4y}, S_{4z} \rangle$  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  $f_2, \dots, f_9$  (the shift in the indexing is motivated by the convention  $f_1 := S_1$ ) for  $\mathcal{Q}'$  is familiar<sup>17</sup>. they consist in two denominator polynomials of the module of  $\mathbb{T}_d$ -invariant polynomials in  $S_{2a}, S_{2b}, \mathbb{R}[S_{2a}, S_{2b}]^{\mathbb{T}_d}$ , three denominator polynomials of  $\mathbb{R}[S_{3x}, S_{3y}, S_{3z}]^{\mathbb{T}_d}$  and of three denominator polynomials of  $\mathbb{R}[S_{4x}, S_{4y}, S_{4z}]^{\mathbb{T}_d}$ . We list them below by degrees of increasing order:

1. Degree 2:

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

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

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

2. Degree 3:

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

$$f_6 := S_{3x} S_{3y} S_{3z} \quad (11)$$

$$f_7 := S_{4x} S_{4y} S_{4z} \quad (12)$$

3. Degree 4:

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

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

### B. Numerator polynomials of the integrity bases

The Molien series for the action of  $\mathbb{T}_d$  on  $\mathcal{Q}'$  can be directly computed using Burnside's generalization<sup>48</sup> of the Molien's results<sup>45</sup>. 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  $M^G(\Gamma_f; \mathcal{Q}_{a_1} \oplus \dots \oplus \mathcal{Q}_{a_i}; t)$  and the corresponding polynomial is built by coupling previously obtained polynomials with Clebsch–Gordan coefficients of the group  $\mathbb{T}_d$ .

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),

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

with

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

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  $M^{\mathbb{T}_d}(E; F_2 \oplus F_2)$  are built by coupling through Clebsch–Gordan coefficients the numerator polynomial of degree zero in the integrity basis associated to  $M^{\mathbb{T}_d}(A_1; F_2; t_3)$  with the numerator polynomials of degree two and four in the integrity basis associated to  $M^{\mathbb{T}_d}(E; F_2; t_4)$  and two others are obtained by reversing the part of  $M^{\mathbb{T}_d}(A_1; F_2; t_3)$  and  $M^{\mathbb{T}_d}(E; F_2; t_4)$ . 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 successive 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:

## IV. CONCLUSION

$$M^{T_d}(F_2; \mathcal{Q}'; t) = \frac{\mathcal{N}(F_2; \mathcal{Q}'; t)}{(1-t^2)^3(1-t^3)^3(1-t^4)^2}, \quad (15)$$

with

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

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),  $g_1^{F_2,z}, \dots, g_{432}^{F_2,z}$  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  $S_1, \dots, S_{4z}$  coordinates will identify with a unique linear combination of monomials:

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

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

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.<sup>7</sup>. 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.<sup>7</sup>. 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<sup>15,32</sup>. 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<sup>37,50</sup>. 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.

We have determined for the first time integrity bases of the  $\Gamma_f$ -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  $\Gamma_f$ -covariant numerator polynomials given in supplementary material<sup>41</sup>. 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  $\Gamma_f$ . 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  $\Gamma_f$ -covariants is general since the  $\Gamma_f$ -covariant polynomials admit a Hironaka decomposition<sup>43</sup> 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<sup>38</sup>, 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  $M^{T_d}(\Gamma_f; \Gamma_i; t)$ , where  $\Gamma_i$  and  $\Gamma_f$  are irreps. of the group  $T_d$ . The coefficient  $c_n$  in the Taylor expansion  $c_0 + c_1 t + c_2 t^2 + \dots$  of the generating function gives the number of linearly independent  $\Gamma_f$ -covariant polynomials of degree  $n$  that

TABLE I: Numbers  $n_k^{\Gamma_f}$  of  $\Gamma_f$ -covariant numerator polynomials of degree  $k$  and dimensions  $\dim \mathcal{P}_k^{\Gamma_f, i}$ ,  $1 \leq i \leq [\Gamma_f]$ , of the vector spaces of  $\Gamma_f, i$ -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  $\Gamma_f$ -covariant numerator polynomials is equal to  $[\Gamma_f] \times \Pi_j d_j / |G|$ , where  $[\Gamma_f]$  is the dimension of the irreducible representation  $\Gamma_f$ ,  $|G| = 24$  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.<sup>24</sup>. It suffices to multiply the left-hand side of Eq. (2.3.4) by the complex conjugate of the character of  $\pi$  and to notice that this equals to  $[\Gamma_f]$  for  $\pi = Id$ , see also Proposition 4.9 of Ref.<sup>43</sup>.

$\Gamma_f:$ Degree $k$	$A_1$		$A_2$		$E$		$F_1$		$F_2$	
	$n_k^{A_1}$	$\dim \mathcal{P}_k^{A_1}$	$n_k^{A_2}$	$\dim \mathcal{P}_k^{A_2}$	$n_k^E$	$\dim \mathcal{P}_k^{E, i}$	$n_k^{F_1}$	$\dim \mathcal{P}_k^{F_1, i}$	$n_k^{F_2}$	$\dim \mathcal{P}_k^{F_2, i}$
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	
Total	144	$\infty$	144	$\infty$	288	$\infty$	432	$\infty$	432	$\infty$



can be constructed from the objects in the initial  $\Gamma_i$  representation.

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

$$M^{\text{T}d}(\Gamma_f; \Gamma_i; t) = \frac{\mathcal{N}(\Gamma_f; \Gamma_i; t)}{\mathcal{D}(\Gamma_i; t)} = \frac{\sum_{k=1}^N t^{\nu_k}}{\prod_{k=1}^D (1 - t^{\delta_k})}, \quad (\text{A.1})$$

with  $\nu_k \in \mathbb{N}$  and  $\delta_k \in \mathbb{N} \setminus \{0\}$ . The polynomial associated to a  $(1 - t^{\delta_k})$  term in the denominator is an invariant called a denominator polynomial of degree  $\delta_k$  and is noted  $I^{(\delta_k)}(\Gamma_i)$ . The polynomial associated to a  $t^{\nu_k}$  term in the numerator is a  $\Gamma_f$ -covariant called a numerator polynomial of degree  $\nu_k$  and is noted  $E^{(\nu_k)}(\Gamma_f; \Gamma_i)$  (when  $\Gamma_f$  is degenerate,  $E^{(\nu_k)}(\Gamma_f; \Gamma_i)$  will be a vector gathering all the  $\Gamma_f, i$ -covariant numerator polynomials of degree  $\nu_k$  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  $M^{\text{T}d}(\Gamma_f; \Gamma_i; t)$ .

The notation for denominator and numerator polynomials using  $\alpha, \beta, \gamma$  symbols for a chosen basis of the irreps. closely follows the paper of Patera, Sharp and Winternitz<sup>47</sup>. 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<sup>47</sup>, the following relation hold:

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

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  $M^{\text{T}d}(\Gamma_4; \Gamma_4; t)$ . 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  $M^{\text{T}d}(\Gamma_5; \Gamma_4; t)$  due to relation (A.3).

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

A complete list of tables of both denominator and numerator polynomials for all the initial  $\Gamma_i$  and final  $\Gamma_f$  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  $\mathcal{D}(E; t) = (1 - t^2)(1 - t^3)$ . 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  $\mathcal{D}(F_1; t) = (1 - t^2)(1 - t^4)(1 - t^6)$ . 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

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

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

$$E^{(3)}(A_2; F_1) = \alpha\beta\gamma$$

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

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

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

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

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

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

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

$$E^{(1)}(F_1; F_1) = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

$$E^{(3)}(F_1; F_1) = \begin{pmatrix} \alpha^3 \\ \beta^3 \\ \gamma^3 \end{pmatrix}$$

$$E^{(4)}(F_1; F_1) = \frac{1}{\sqrt{2}} \begin{pmatrix} (\beta^2 - \gamma^2)\beta\gamma \\ (\gamma^2 - \alpha^2)\gamma\alpha \\ (\alpha^2 - \beta^2)\alpha\beta \end{pmatrix}$$

$$E^{(5)}(F_1; F_1) = \begin{pmatrix} \alpha^5 \\ \beta^5 \\ \gamma^5 \end{pmatrix}$$

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

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

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

$$E^{(2)}(F_2; F_1) = \begin{pmatrix} \beta\gamma \\ \gamma\alpha \\ \alpha\beta \end{pmatrix}$$

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

$$E^{(4)}(F_2; F_1) = \alpha\beta\gamma \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

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

$$E^{(6)}(F_2; F_1) = \alpha\beta\gamma \begin{pmatrix} \alpha^3 \\ \beta^3 \\ \gamma^3 \end{pmatrix}$$

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

## 5. $\Gamma_i = F_2$ irreducible representation

The denominator is  $\mathcal{D}(F_2; t) = (1 - t^2)(1 - t^3)(1 - t^4)$ . 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

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

the two  $E$ -covariant numerator polynomials of degree two and four are

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

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

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

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

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

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

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

$$E^{(1)}(F_2; F_2) = \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

$$E^{(2)}(F_2; F_2) = \begin{pmatrix} \beta\gamma \\ \gamma\alpha \\ \alpha\beta \end{pmatrix}$$

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

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