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A Fast Algorithm for the Construction of Integrity Bases Associated to Symmetry–Adapted Polynomial Representations. Application to Tetrahedral XY_4 Molecules

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Invariant theory provides more efficient tools, such as Molien generating functions and integrity bases, than basic group theory, that relies on projector techniques for the construction of symmetry–adapted polynomials in the symmetry coordinates of a molecular system, because it is based on a finer description of the mathematical structure of the latter. The present article extends its use to the construction of polynomial bases which span possibly, non–totally symmetric irreducible representations of a molecular symmetry group. Electric or magnetic observables can carry such irreducible representations, a common example is given by the electric dipole moment surface. The elementary generating functions and their corresponding integrity bases, where both the initial and the final representations are irreducible, are the building blocks of the algorithm presented in this article, which is faster than algorithms based on projection operators only. The generating functions for the full initial representation of interest are built recursively from the elementary generating functions. Integrity bases which can be used to generate in the most economical way symmetry–adapted polynomial bases are constructed alongside in the same fashion. The method is illustrated in detail on XY_4 type of molecules. Explicit integrity bases for all five possible final irreducible representations of the tetrahedral group have been calculated and are given in the supplemental material associated with this paper.

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I. INTRODUCTION

The simulation of the rotation–vibration molecular spectrum 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 issue is often encountered in quantum chemistry or computational spectroscopy and a typical solution is to expand these functions on a set of appropriate analytical functions. The expansion coefficients are then determined by fitting over experimental or theoretical data. 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 (irrep) of the symmetry group G of the molecule. In particular, the PES transforms as the totally symmetric (also called trivial) irrep 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 spans a representation called the initial, usually reducible, representation Γ^{initial}. Symmetry–adapted polynomials in these variables are then considered. The polynomials that transform according to the final irrep Γ^{final} are called Γ^{final}–covariant polynomials.[6] An "invariant" polynomial is the distinct case of this classification when Γ^{final} is the totally symmetric representation of the group, noted A, A', A_1, or A_g in character tables.

Projecting on irreps using projection operators is a standard method of group theory to generate symmetry–adapted polynomials. Marquardt[7] and Schwenke[8] relied on this technique to compute symmetry–adapted basis sets and expand the PES of methane. The projection method for the construction of invariants is applicable to 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 projectors 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 symmetry–adapted polynomials is based on the Clebsch–Gordan coefficients of the group G. A great deal of work has been dedicated in particular to the cubic group.[12–15] The coupling with 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 space basis sets of polynomials of lower degrees must be considered to insure that one gets a complete list. Compared to the previous approach based on projection operators, the computational effort is reduced but the tabulated basis sets have the same unnecessarily large sizes.

The drawbacks of the two approaches described above are circumvented by polynomial ring invariant theory, which in spite of its name encompasses the covariant case and fully exploits the algebraic structure of Γ^{final}–covariant polynomials. In particular, the coefficient c_k of the Taylor expansion $c_0 + c_1 t + c_2 t^2 + c_3 t^3 + \cdots$ of the Molien generating function[16,17] gives the number of linearly independent polynomials of degree k carrying a given symmetry. 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] Recently, Braams, Bowman and their collaborators introduced permutationally invariant polynomial bases that satisfy the permutational symmetry with respect to like atoms.[22–24] 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 Γ^{final}–covariant polynomials involves two finite sets of polynomials.[16,25] The first set contains D *denominator* or *primary* polynomials f_i, $1 \leq i \leq D$, which are algebraically independent invariant polynomials.[16,26] The second set contains N linearly independent *numerator* or *secondary* polynomials g_j, $1 \leq j \leq N$, which transform as the Γ^{final} representation. Any Γ^{final}–covariant polynomial p admits a unique decomposition in the denominator and numerator polynomials: $p = g_1 \times h_1\left(f_1, \ldots, f_D\right) + \cdots + g_N \times h_N\left(f_1, \ldots, f_D\right)$. The h_j are polynomials in D variables: any nonnegative integer can be a power of the denominator polynomials while numerator polynomials only appear linearly. The important result is that the integrity basis is a much more compact way to present the set of Γ^{final}–covariant polynomials than a list of vector space bases for each degree k. All the Γ^{final}–covariant polynomials, up to any order, can be generated from the polynomials be-

longing to the small integrity basis by a direct algorithm. This circumvents the problems inherent to projector or Clebsch–Gordan based methods, where gigantic tables necessarily limited to a given (usually low) degree have to be stored. Applications of integrity bases are numerous. They have been used to define error–correcting codes in applied mathematics,[27] to analyze problems involving crystal symmetry,[28,29] constitutive equations in materials with symmetry,[30–32] physical systems of high–energy physics[33,34] and molecular physics,[16,18,35] the description of qubits,[36,37] ...

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. In contrast, in the present paper we are only dealing with finite groups. 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).[25,38,39] This is a remarkable difference with respect to the algebraic structure of invariants. The non–free modules of SO(2) have been discussed in[25] and a forthcoming article will be devoted to the study of covariant modules of the SO(3) group.[40]

The focus of the present article is on the Γ^{final}–covariants built from symmetry coordinates for the tetrahedral point group T_d, although the techniques employed would work for any finite 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),[41,42] Cartesian normal coordinates,[41,43–47] 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,[48] cosines of valence bond angles times functions of bond lengths,[49] symmetrized coordinates based on bond lengths, interbond angles and torsion angles,[15] or interbond angles and bond lengths times a gaussian exponential factor.[50]

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 have been used to obtain a polynomial basis set for totally symmetric quantities can be extended to quantities transforming according to an arbitrary irrep. This is useful to obtain very efficiently a basis set of F_2–symmetry–adapted

polynomials, in the T_d-symmetry group, 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 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.[51] However, on the one hand, existing methods of computational invariant theory[26,52,53] 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 and illustrate its mathematical concepts with a case example of C_i symmetry. Then, we show how the integrity basis of Γ^{final}–covariant polynomials in the T_d point group can be constructed recursively for XY_4 molecules, $\Gamma^{\text{final}} \in \{A_1, A_2, E, F_1, F_2\}$. The resulting minimal generating families of symmetry–adapted functions are listed in the supplemental material.[54] In conclusion, we emphasize that our approach is general, as only minor points 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 book by Benson[55] and the article of Stanley.[56] Schmelzer and Murrell[19] have had a pioneering influence as far as the construction of a PES is concerned. The review of Michel and Zhilinskií[16] gives 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 any invariant or Γ^{final}–covariant polynomials has a general decomposition. We refer to Stanley[56] 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. This algebra is a direct sum of vector spaces $\mathcal{P}_n$ of polynomials of degree n: $\mathcal{P} = \bigoplus_{n\geq 0} \mathcal{P}_n$. We assume that the finite group G acts linearly on the vector space $< Q_1, \ldots, Q_k >$ spanned by $Q_1, \ldots, Q_k$. This action extends naturally to $\mathcal{P}$.

Let $\mathcal{P}^{\Gamma^{\rm final}} \subset \mathcal{P}$ be the vector subspace of polynomials transforming as the irrep $\Gamma^{\rm final}$ and let $\left[\Gamma^{\rm final}\right]$ be the dimension of the irrep $\Gamma^{\rm final}$. This integer equals 1, 2 or 3 for most of the point groups except for the icosahedral point groups I and $\rm I_h$ where irreps of dimensions 4 and 5 occur. A representation of dimension greater than one is qualified as *degenerate*. It is convenient to assume for the forthcoming developments that the representation $\Gamma^{\rm final}$ has a distinguished basis $\psi^{\Gamma^{\rm final},1}, ..., \psi^{\Gamma^{\rm final},\left[\Gamma^{\rm final}\right]}$. A polynomial $\varphi^{\Gamma^{\rm final}} \in \mathcal{P}^{\Gamma^{\rm final}}$ is then further decomposed as a sum over $\left[\Gamma^{\rm final}\right]$ polynomials,

$$\varphi^{\Gamma^{\rm final}} = \sum_{i=1}^{\left[\Gamma^{\rm final}\right]} \varphi^{\Gamma^{\rm final},i}, \tag{1}$$

each term $\varphi^{\Gamma^{\rm final},i}$ behaving as the basis function $\psi^{\Gamma^{\rm final},i}$ under the action of the group G, see e.g. equation (3-187) of Hamermesh.[9] The symmetry type of the polynomial $\varphi^{\Gamma^{\rm final},i}$ is written $\Gamma^{\rm final}, i$. We deduce, $\mathcal{P}^{\Gamma^{\rm final}} = \bigoplus_{i=1}^{\left[\Gamma^{\rm final}\right]} \mathcal{P}^{\Gamma^{\rm final},i}$ from the decomposition, eq (1), for the vector space of $\Gamma^{\rm final}$–covariant polynomials.

An important mathematical result is that there exists exactly k algebraically independent invariant polynomials $\{f_1, \ldots, f_k\}$ and a finite number $p_{\Gamma^{\rm final}}$ of linearly independent polynomials of symmetry $\Gamma^{\rm final}, i$: $\left\{g_1^{\Gamma^{\rm final},i}, \ldots, g_{p_{\Gamma^{\rm final}}}^{\Gamma^{\rm final},i}\right\}$, such that

$$\mathcal{P}^{\Gamma^{\rm final},i} = \bigoplus_{j=1}^{p_{\Gamma^{\rm final}}} \mathbb{C}[f_1, \ldots, f_k] g_j^{\Gamma^{\rm final},i},\ i \in \left\{1, 2, \ldots, \left[\Gamma^{\rm final}\right]\right\}, \tag{2}$$

where $\mathbb{C}[f_1, ..., f_k]$ is the algebra spanned by the polynomials $\{f_1, \ldots, f_k\}$. The number $p_{\Gamma^{\rm final}}$ depends on the irrep $\Gamma^{\rm final}$ but is independent on the index i. We refer to the whole set $\{f_1, ..., f_k; g_1^{\Gamma^{\rm final},i}, ..., g_{p_{\Gamma^{\rm final}}}^{\Gamma^{\rm final},i}\}$ as an integrity basis for the module $\mathcal{P}^{\Gamma^{\rm final},i}$. The f_i are called the *denominator* or *primary* polynomials, while the $g_j^{\Gamma^{\rm final}}$ are called the *numerator* or *secondary* polynomials. The same set of primary invariants is used for all the irreps. Such a decomposition as in eq 2 is sometimes referred to as an Hironaka decomposition and

defines a so–called Cohen–Macaulay module. In the particular case where Γ^{final} is the trivial representation (so that Γ^{final}–covariants are simply invariants), this result shows that $\mathcal{P}^{\Gamma^{\text{final}}}$, the algebra of invariant polynomials, is a Cohen–Macaulay algebra.

The elements of the integrity basis can always be chosen homogeneous, and from now on, we assume that this homogeneity property always 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^{final}–covariant basis polynomials and their degrees are fixed and determined by the so–called Molien series.[57] The problem of constructing polynomials of symmetry type Γ^{final}, i from symmetrized coordinates spanning the representation Γ^{initial} leads to consider the Molien series, $M^G\left(\Gamma^{\text{final}}; \Gamma^{\text{initial}}; t\right)$, defined by:

$$M^G\left(\Gamma^{\text{final}}; \Gamma^{\text{initial}}; t\right) = \sum_{n \geq 0} \dim \mathcal{P}_n^{\Gamma^{\text{final}},i}\ t^n, \tag{3}$$

where $\mathcal{P}_n^{\Gamma^{\text{final}},i} = \mathcal{P}^{\Gamma^{\text{final}},i} \cap \mathcal{P}_n$ is the vector space of polynomials of symmetry type Γ^{final}, i and of degree n. In other words, the coefficient $\dim \mathcal{P}_n^{\Gamma^{\text{final}},i}$ of the Molien series gives the number of linearly independent polynomials of symmetry type Γ^{final}, i and of degree n.

Suppose that $\{f_1, ..., f_k; g_1^{\Gamma^{\text{final}},i}, ..., g_{p_{\Gamma^{\text{final}}}}^{\Gamma^{\text{final}},i}\}$ is an integrity basis for $\mathcal{P}^{\Gamma^{\text{final}},i}$. Then it can be shown that the corresponding Molien series can be cast in the following form:

$$M^G\left(\Gamma^{\text{final}}; \Gamma^{\text{initial}}; t\right) = \frac{t^{\deg(g_1^{\Gamma^{\text{final}},i})} + \cdots + t^{\deg(g_{p_{\Gamma^{\text{final}}}}^{\Gamma^{\text{final}},i})}}{\left(1 - t^{\deg(f_1)}\right) \cdots \left(1 - t^{\deg(f_k)}\right)}, \tag{4}$$

where $\deg(p)$ is the degree of the polynomial p (the degrees are not necessarily all distinct in this expression). The expression of the Molien function $M^G\left(\Gamma^{\text{final}}; \Gamma^{\text{initial}}; t\right)$ is independent of the choice of the index i. The right–hand side of eq 4 justifies the alternative denomination of the f_i primary polynomials as *denominator* polynomials and of the $g_j^{\Gamma^{\text{final}},i}$ secondary polynomials as *numerator* polynomials. Once the degrees of the denominator invariants are given and the Molien function calculated, the number of numerator polynomials of each degree is given by the corresponding coefficient in the polynomial $M^G\left(\Gamma^{\text{final}}; \Gamma^{\text{initial}}; t\right) \times (1 - t^{\deg(f_1)}) \cdots (1 - t^{\deg(f_k)})$. The problem of generating the module $\mathcal{P}^{\Gamma^{\text{final}},i}$ comes down to the computation of a complete set of such numerator polynomials given a set of denominator invariants.

B. Recursive construction

1. Generating function

We considered in the previous section the action of a finite group G on a polynomial algebra $\mathcal{P}$ over a vector space $< Q_1, \ldots, Q_k >$. In our applications of invariant theory, the representation Γ^{initial} spanned by the symmetrized coordinates typically splits into a direct sum of μ irreps $\Gamma_i^{\text{initial}}$, $1 \leq i \leq \mu$,

$$\Gamma^{\text{initial}} = \bigoplus_{i=1}^{\mu} \Gamma_i^{\text{initial}}.$$

The definition of the Molien series in eq 3 of Section II A involved only one variable t. In order to follow the contributions of the different irreps $\Gamma_i^{\text{initial}}$, we introduce now one t_i variable for each $\Gamma_i^{\text{initial}}$ and write $M^G\left(\Gamma; \Gamma_1^{\text{initial}} \oplus \Gamma_2^{\text{initial}} \oplus \cdots \oplus \Gamma_k^{\text{initial}}; t_1, t_2, \ldots, t_k\right)$ for the Molien series associated to Γ–covariants polynomials in the variables contained in the reducible irrep $\Gamma_1^{\text{initial}} \oplus \Gamma_2^{\text{initial}} \oplus \cdots \oplus \Gamma_k^{\text{initial}}$ under group G.

Let us note $c^{\Gamma}_{\Gamma_\alpha,\Gamma_\beta}$ for the multiplicity of the irrep Γ in the direct (or Kronecker) product $\Gamma_\alpha \times \Gamma_\beta$ of the irreps Γ_α and Γ_β. In case of the T_d point group, $c^{\Gamma}_{\Gamma_\alpha,\Gamma_\beta} = 0$ or 1, see Wilson *et al.*.[1] Decomposing the initial reducible representation Γ^{initial} as

$$\Gamma^{\text{initial}} = \left(\Gamma_1^{\text{initial}} \oplus \cdots \oplus \Gamma_{\mu-1}^{\text{initial}}\right) \oplus \Gamma_\mu^{\text{initial}},$$

(note the parentheses), the generating function $M^G\left(\Gamma; \Gamma^{\text{initial}}; t_1, t_2, \ldots, t_\mu\right)$ can be built by coupling the generating functions

$$M^G\left(\Gamma_\alpha; \Gamma_1^{\text{initial}} \oplus \Gamma_2^{\text{initial}} \oplus \cdots \oplus \Gamma_{\mu-1}^{\text{initial}}; t_1, t_2, \ldots, t_{\mu-1}\right),$$

with the generating functions

$$M^G\left(\Gamma_\beta; \Gamma_\mu^{\text{initial}}; t_\mu\right),$$

where Γ_α and Γ_β are irreps, (see Equation (46) of Michel and Zhilinskií[16] and Appendix A,) according to the following equation:

$$M^G\left(\Gamma; \Gamma_1^{\text{initial}} \oplus \Gamma_2^{\text{initial}} \oplus \cdots \oplus \Gamma_{\mu-1}^{\text{initial}} \oplus \Gamma_\mu^{\text{initial}}; t_1, t_2, \ldots, t_{\mu-1}, t_\mu\right) =$$
$$\sum_{\Gamma_\alpha,\Gamma_\beta} c^{\Gamma}_{\Gamma_\alpha,\Gamma_\beta} M^G\left(\Gamma_\alpha; \Gamma_1^{\text{initial}} \oplus \Gamma_2^{\text{initial}} \oplus \cdots \oplus \Gamma_{\mu-1}^{\text{initial}}; t_1, t_2, \ldots, t_{\mu-1}\right) \times M^G\left(\Gamma_\beta; \Gamma_\mu^{\text{initial}}; t_\mu\right) \quad (5)$$

In eq 5, the double sum on Γ_α and Γ_β runs over all the irreps of the group G. The Molien function $M^G\left(\Gamma_\alpha;\Gamma_1^{\text{initial}}\oplus\Gamma_2^{\text{initial}}\oplus\cdots\oplus\Gamma_{\mu-1}^{\text{initial}};t_1,t_2,\ldots,t_{\mu-1}\right)$ in the right–hand side of eq 5 can itself be computed through an equation similar to eq 5 if the representation $\Gamma_1^{\text{initial}}\oplus\Gamma_2^{\text{initial}}\oplus\cdots\oplus\Gamma_{\mu-1}^{\text{initial}}$ is seen as a direct sum of $\Gamma_1^{\text{initial}}\oplus\Gamma_2^{\text{initial}}\oplus\cdots\oplus\Gamma_{\mu-2}^{\text{initial}}$ and $\Gamma_{\mu-1}^{\text{initial}}$. These iterations are continued until no more decomposition of the representations is possible. The left–hand side of eq 5 is then ultimately written as a sum of products of *elementary generating functions* $M^G\left(\Gamma_\alpha;\Gamma_i^{\text{initial}};t_i\right)$ where both Γ_α and $\Gamma_i^{\text{initial}}$ are irreps. Such elementary generating functions have already appeared in the litterature for a variety of point groups[58], (see also Appendix A). These elementary generating functions are the building blocks required to compute recursively according to eq 5, the Molien generating function of the problem under study.

2. Integrity basis

To each generating function of the form, eq 4, correspond integrity bases whose number and degree of the denominator and numerator polynomials are suggested by such an expression. Let

$$\bigcup_{x\in\{1,2,\cdots,[\Gamma_\alpha]\}}\{f_1,...,f_k;g_1^{\Gamma_\alpha,x},...,g_{p_{\Gamma_\alpha}}^{\Gamma_\alpha,x}\},$$

be an integrity basis corresponding to the generating function

$$M^G\left(\Gamma_\alpha;\Gamma_1^{\text{initial}}\oplus\cdots\oplus\Gamma_{i-1}^{\text{initial}};t_1,\ldots,t_{i-1}\right), \tag{6}$$

and let

$$\bigcup_{y\in\left\{1,2,\cdots,\left[\Gamma_\beta\right]\right\}}\{h_1,...,h_l;j_1^{\Gamma_\beta,y},...,j_{p_{\Gamma_\beta}}^{\Gamma_\beta,y}\},$$

be an integrity basis corresponding to the generating function

$$M^G\left(\Gamma_\beta;\Gamma_i^{\text{initial}};t_i\right). \tag{7}$$

The f_i and $g_j^{\Gamma_\alpha,x}$ are polynomials in the variables of the representation $\Gamma_1^{\text{initial}}\oplus\cdots\oplus\Gamma_{i-1}^{\text{initial}}$, while the h_i and $j_j^{\Gamma_\beta,y}$ are polynomials in the variables of the representation $\Gamma_i^{\text{initial}}$.

The set $\{f_1,...,f_k,h_1,...,h_l\}$ is the set of denominator or primary invariants for the generating function

$$M^G\left(\Gamma;\Gamma_1^{\text{initial}}\oplus\cdots\oplus\Gamma_{i-1}^{\text{initial}}\oplus\Gamma_i^{\text{initial}};t_1,\ldots,t_{i-1},t_i\right). \tag{8}$$

The numerator or secondary polynomials of the generating function of eq 8 are generated by coupling the numerator polynomials $g_a^{\Gamma_\alpha,1}$, ..., $g_a^{\Gamma_\alpha,[\Gamma_\alpha]}$ with the numerator polynomials $j_b^{\Gamma_\beta,1}$, ..., $j_b^{\Gamma_\beta,[\Gamma\beta]}$ via the Clebsch–Gordan coefficients of the group G for all $(\Gamma_\alpha, \Gamma_\beta)$ pairs such that $\Gamma \in \Gamma_\alpha \times \Gamma_\beta$, see Section 5.6 of Hamermesh.[9] We write these functions $m^{\Gamma,\kappa}_{\Gamma_\alpha,\Gamma_\beta,a,b,i}$, where $1 \le i \le c^{\Gamma}_{\Gamma_\alpha,\Gamma_\beta}$, $1 \le a \le p_{\Gamma_\alpha}$, $1 \le b \le p_{\Gamma_\beta}$, and $\kappa \in \{1, 2, \cdots, [\Gamma]\}$. The resulting integrity basis corresponding to eq 8 can be expressed as

$$\{f_1, ..., f_k, h_1, ..., h_l; \bigcup_{\Gamma_\alpha,\Gamma_\beta} \{m^{\Gamma,\kappa}_{\Gamma_\alpha,\Gamma_\beta,a,b,i}, 1 \le a \le p_{\Gamma_\alpha}, 1 \le b \le p_{\Gamma_\beta}, 1 \le i \le c^{\Gamma}_{\Gamma_\alpha,\Gamma_\beta}, \kappa \in \{1, 2, \cdots, [\Gamma]\}\},$$

(if $\Gamma \notin \Gamma_\alpha \times \Gamma_\beta$, $c^{\Gamma}_{\Gamma_\alpha,\Gamma_\beta} = 0$, and the set of $m^{\Gamma,\kappa}_{\Gamma_\alpha,\Gamma_\beta,a,b,i}$'s is empty).

So, the integrity basis is built in a straightforward manner from integrity bases associated to generating functions eqs (6) and (7), where both initial representations are of smaller dimensions. Iterating this process constitutes an effective algorithm which only needs the elementary generating functions of group G for its initialization. The latter functions have already been tabulated[58] for most groups of interest. The algorithm terminates when all $\Gamma_i^{\text{initial}}$'s have been incorporated.

C. Illustration on a case example

The present section gives a straightforward application of the recursive construction in the simplest non trivial case of the two-element group, which can be taken as the C_i group used in chemistry for molecular structures with a center of inversion.

1. Group C_i

The group C_i has two elements: the identity operation E leaves unchanged the coordinates of the particles, $x \mapsto x$, while the inversion operation I changes the sign of the coordinates, $x \mapsto -x$. The character table of the C_i group is given in Table I and shows that two one–dimensional irreps A_1 and A_2 occur in this group.

TABLE I. Character table of the C_i point group.

	E	I
A_1	1	1
A_2	1	−1

2. *Elementary generating functions*

Applications of group theory often search to construct objects that transforms as a final irrep Γ^{final} of a group G from elementary objects that spans an initial, possibly reducible, representation Γ^{initial}. If these objects are polynomials, we can sort them by their degree and count the number c_k of linearly independent polynomials of degree k that can be built up. The information on the c_k's is encoded into the so–called Molien series or generating function:

$$M^G\left(\Gamma^{\text{final}};\Gamma^{\text{initial}};t\right) = c_0 + c_1 t + c_2 t^2 + c_3 t^3 + \cdots. \tag{9}$$

Elementary generating functions are particular generating functions when both the initial representation Γ^{initial} and the final representation Γ^{final} are irreps of the group. The group $\mathrm{C_i}$ has two irreps and thus four elementary generating functions have to be considered: $M^{\mathrm{C_i}}\left(A_1;A_1;t\right)$, $M^{\mathrm{C_i}}\left(A_2;A_1;t\right)$, $M^{\mathrm{C_i}}\left(A_1;A_2;t\right)$, and $M^{\mathrm{C_i}}\left(A_2;A_2;t\right)$.

3. $M^{\mathrm{C_i}}\left(\Gamma^{\text{final}};A_1;t\right)$

The absolute value $|x|$ is a good example of an A_1–symmetric (invariant) object as it does not change sign under neither the identity E nor the inversion I operations. From $|x|$ can be constructed one invariant of degree 0 ($|x|^0 = 1$), one invariant of degree 1 ($|x|^1$), one invariant of degree two ($|x|^2$), and more generally, one invariant of degree k ($|x|^k$). However, no object of symmetry A_2 can be constructed from $|x|$. As a consequence, we can write as in eq 9 the expressions of the Molien series $M^{\mathrm{C_i}}\left(\Gamma^{\text{final}};A_1;t\right)$:

$$\begin{aligned} M^{\mathrm{C_i}}\left(A_1;A_1;t\right) &= 1 + t + t^2 + t^3 + t^4 + \cdots = \tfrac{1}{1-t}, \\ M^{\mathrm{C_i}}\left(A_2;A_1;t\right) &= 0. \end{aligned} \tag{10}$$

4. $M^{\mathrm{C_i}}\left(\Gamma^{\text{final}};A_2;t\right)$

The monomial x is an example of an A_2–symmetric object because it changes sign under the inversion I operation. The even powers of x will be of A_1–symmetry:

$$x^{2n} \mapsto (-x)^{2n} = x^{2n}, \tag{11}$$

while the odd powers of x will be of A_2–symmetry:

$$x^{2n+1} \mapsto (-x)^{2n+1} = -x^{2n+1}. \tag{12}$$

We see that from an A_2–symmetric object can be constructed one object of symmetry A_1 of any even degree and one object of symmetry A_2 of any odd degree. These results are encoded in the two following Molien series:

$$\begin{aligned} M^{\mathrm{C_i}}\left(A_1;A_2;t\right) &= 1+t^2+t^4+t^6+\cdots = \tfrac{1}{1-t^2}, \\ M^{\mathrm{C_i}}\left(A_2;A_2;t\right) &= t+t^3+t^5+t^7+\cdots = \tfrac{t}{1-t^2}. \end{aligned} \tag{13}$$

5. Integrity bases for the elementary generating functions

An integrity basis consists in two sets of polynomials, the denominator and the numerator polynomials. A generating function written as in the right–hand side of eq 4 suggests both the number and the degree of the denominator and numerator polynomials, and is a very valuable source of information when an integrity basis is built up. When forming polynomials that transform as the Γ^{final} irrep from polynomials that belongs to the integrity basis corresponding to $M^G\left(\Gamma^{\mathrm{final}};\Gamma^{\mathrm{initial}};t\right)$, eq 2 indicates that the denominator polynomials can be multiplied between them with no restriction at all while the numerator polynomials only appear linearly. The explicit expressions of the integrity bases for the four elementary generating functions of the group $\mathrm{C_i}$ are given in Table II. For example, the last line of Table II suggests that we can recover all the polynomials of symmetry A_2 built up from x by multiplying the numerator polynomial x with any power of the denominator polynomial x^2. The final result is a polynomial of the form x^{2n+1} which has the desired symmetry, see eq 12.

TABLE II. Integrity bases for the four elementary generating functions of the group $\mathrm{C_i}$.

Generating function	Denominator polynomials	Numerator polynomials
$M^{\mathrm{C_i}}\left(A_1;A_1;t\right)=\frac{1}{1-t}$	$\{\lvert x\rvert\}$	$\{1\}$
$M^{\mathrm{C_i}}\left(A_2;A_1;t\right)=0$		
$M^{\mathrm{C_i}}\left(A_1;A_2;t\right)=\frac{1}{1-t^2}$	$\{x^2\}$	$\{1\}$
$M^{\mathrm{C_i}}\left(A_2;A_2;t\right)=\frac{t}{1-t^2}$	$\{x^2\}$	$\{x\}$

6. *Case example*

Let us consider three particles moving on an infinite straight line under the symmetry group C_i. The position of the three particles are given by x_i, $1 \leq i \leq 3$. The action of the inversion I changes the coordinates of the three particles: $x_i \mapsto -x_i$. The three x_i variables can be seen as polynomials of degree one. They are manifestly of symmetry A_2, hence the initial reducible representation is $\Gamma^{\text{initial}} = A_2 \oplus A_2 \oplus A_2$. Polynomials of higher degree can be built up from the x_1, x_2 and x_3 polynomials and the example is simple enough that the symmetry of the higher degree polynomials is immediately deduced.

The case example is to construct all the polynomials in x_1, x_2, and x_3 of symmetry A_1 or A_2 up to a given degree. This is the kind of problem that appear when the potential energy surface or the electric dipole moment surface are expanded in symmetry–adapted polynomials. Table III gives a list of the linearly independent polynomials of low degree in x_1, x_2, and x_3 that can be found by manual inspection.

TABLE III. Linearly independent polynomials of degree k, $0 \leq k \leq 5$, in variables x_1, x_2, and x_3 transforming according to the irrep Γ^{final}. The number of such polynomials is noted $\dim \mathcal{P}_k^{\Gamma^{\text{final}}}$.

Γ^{final}	k	Polynomials	$\dim \mathcal{P}_k^{\Gamma^{\text{final}}}$
A_1	0	1	1
A_1	2	x_1^2, x_1x_2, x_1x_3, x_2^2, x_2x_3, x_3^2	6
A_1	4	x_1^4, $x_1^3x_2$, $x_1^3x_3$, $x_1^2x_2^2$, $x_1^2x_2x_3$, $x_1^2x_3^2$, $x_1x_2^3$, $x_1x_2^2x_3$, $x_1x_2x_3^2$, $x_1x_3^3$, x_2^4, $x_2^3x_3$, $x_2^2x_3^2$, $x_2x_3^3$, x_3^4	15
A_2	1	x_1, x_2, x_3	3
A_2	3	x_1^3, $x_1^2x_2$, $x_1^2x_3$, $x_1x_2^2$, $x_1x_2x_3$, $x_1x_3^2$, x_2^3, $x_2^2x_3$, $x_2x_3^2$, x_3^3	10
A_2	5	x_1^5, $x_1^4x_2$, $x_1^4x_3$, $x_1^3x_2^2$, $x_1^3x_2x_3$, $x_1^3x_3^2$, $x_1^2x_2^3$, $x_1^2x_2^2x_3$, $x_1^2x_2x_3^2$, $x_1^2x_3^3$, $x_1x_2^4$, $x_1x_2^3x_3$, $x_1x_2^2x_3^2$, $x_1x_2x_3^3$, $x_1x_3^4$, x_2^5, $x_2^4x_3$, $x_2^3x_3^2$, $x_2^2x_3^3$, $x_2x_3^4$, x_3^5	21

From the last column of Table III and remembering that the coefficient c_k in eq 9 is the number of linearly independent polynomials of degree k for a given final symmetry, the generating functions are found to be:

$$M^{C_i}\left(A_1; \Gamma^{\text{initial}}; t\right) = 1 + 6t^2 + 15t^4 + \cdots, \tag{14}$$

for the $\Gamma^{\text{final}} = A_1$ representation, and

$$M^{\mathrm{C_i}}\left(A_1;\Gamma^{\text{initial}};t\right) = 3t + 10t^3 + 21t^5 + \cdots, \tag{15}$$

or the $\Gamma^{\text{final}} = A_2$ representation.

These generating functions can be directly computed using the Molien's formula and Burnside's generalization to final irrep different from the totally symmetry one.[57,59] For a finite point group G, the Molien function reads:

$$M^{G}\left(\Gamma^{\text{final}};\Gamma^{\text{initial}};t\right) = \frac{1}{|G|}\sum_{g\in G}\frac{\bar{\chi}\left(\Gamma^{\text{final}};g\right)}{\det\left(1_{n\times n} - tM\left(\Gamma^{\text{initial}};g\right)\right)}, \tag{16}$$

where $|G|$ is the order of G, $\bar{\chi}\left(\Gamma^{\text{final}};g\right)$ is the complex conjugate of the character for element $g \in G$ and irrep Γ^{final}, $1_{n\times n}$ is the $n \times n$ identity matrix acting on Γ^{initial} of dimension n, $M\left(\Gamma^{\text{initial}};g\right)$ is the $n \times n$ matrix representation of g on Γ^{initial}, and det is the determinant of a matrix.

In our example, the representation matrices of the $\Gamma^{\text{initial}} = A_2 \oplus A_2 \oplus A_2$ are the two 3×3 diagonal matrices: $M\left(\Gamma^{\text{initial}};E\right) = \mathrm{diag}\left(1,1,1\right)$ and $M\left(\Gamma^{\text{initial}};I\right) = \mathrm{diag}\left(-1,-1,-1\right)$. Using Table I, the representation matrices and Molien's formula 16, we find the two generating functions:

$$M^{\mathrm{C_i}}\left(A_1;\Gamma^{\text{initial}};t\right) = \frac{1+3t^2}{\left(1-t^2\right)^3}, \tag{17}$$

$$M^{\mathrm{C_i}}\left(A_2;\Gamma^{\text{initial}};t\right) = \frac{3t+t^3}{\left(1-t^2\right)^3}. \tag{18}$$

It can be checked that the Taylor series of eqs 17 and 18 around $t = 0$ correspond to the expansion whose beginning is given in eqs 14 and 15. The generating function eq 17 suggests that the integrity basis for the invariants built from x_1, x_2, and x_3 consists of three denominator polynomials of degree two and four numerator polynomials, of which one is of degree zero and three are of degree two. Eq 18 suggests that the integrity basis for the polynomials of symmetry A_2 consists of three denominator polynomials of degree two and four numerator polynomials, of which three are of degree one and one is of degree three.

7. Recursive construction of the generating functions

Eqs 17 and 18 were obtained from Molien's formula 16. However, they can be derived more efficiently from the recursive construction of section II B.

Let us use eq 5 to compute recursively the generating functions for our case example from the elementary generating functions of $\mathrm{C_i}$. Noting the direct products $A_1 \times A_1 = A_2 \times A_2 = A_1$ and $A_1 \times A_2 = A_2 \times A_1 = A_2$, only four $c^{\Gamma}_{\Gamma_\alpha,\Gamma_\beta}$ coefficients do not vanish:

$$c^{A_1}_{A_1,A_1} = c^{A_1}_{A_2,A_2} = c^{A_2}_{A_1,A_2} = c^{A_2}_{A_2,A_1} = 1. \tag{19}$$

The generating function for the invariant polynomials in x_1, x_2, and x_3 is, according to eqs 5 and 19:

$$\begin{aligned} &M^{\mathrm{C_i}}\left(A_1; A_2 \oplus A_2 \oplus A_2; t_1, t_2, t_3\right) \\ &= M^{\mathrm{C_i}}\left(A_1; A_2 \oplus A_2; t_1, t_2\right) M^{\mathrm{C_i}}\left(A_1; A_2; t_3\right) \\ &\quad + M^{\mathrm{C_i}}\left(A_2; A_2 \oplus A_2; t_1, t_2\right) M^{\mathrm{C_i}}\left(A_2; A_2; t_3\right). \end{aligned}$$

Each of the $M^{\mathrm{C_i}}\left(\Gamma_\alpha; A_2 \oplus A_2; t_1, t_2\right)$ term can again be decomposed using eq 5, and we finally find a relation where only elementary generating functions appear in the right–hand side:

$$\begin{aligned} &M^{\mathrm{C_i}}\left(A_1; A_2 \oplus A_2 \oplus A_2; t_1, t_2, t_3\right) \\ &= M^{\mathrm{C_i}}\left(A_1; A_2; t_1\right) M^{\mathrm{C_i}}\left(A_1; A_2; t_2\right) M^{\mathrm{C_i}}\left(A_1; A_2; t_3\right) \\ &\quad + M^{\mathrm{C_i}}\left(A_2; A_2; t_1\right) M^{\mathrm{C_i}}\left(A_2; A_2; t_2\right) M^{\mathrm{C_i}}\left(A_1; A_2; t_3\right) \\ &\quad + M^{\mathrm{C_i}}\left(A_1; A_2; t_1\right) M^{\mathrm{C_i}}\left(A_2; A_2; t_2\right) M^{\mathrm{C_i}}\left(A_2; A_2; t_3\right) \\ &\quad + M^{\mathrm{C_i}}\left(A_2; A_2; t_1\right) M^{\mathrm{C_i}}\left(A_1; A_2; t_2\right) M^{\mathrm{C_i}}\left(A_2; A_2; t_3\right). \end{aligned} \tag{20}$$

The expressions of the elementary generating functions are given in eqs 10 and 13, and the expression for the invariants reads as:

$$M^{\mathrm{C_i}}\left(A_1; A_2 \oplus A_2 \oplus A_2; t_1, t_2, t_3\right) = \frac{1 + t_1 t_2 + t_1 t_3 + t_2 t_3}{\left(1 - t_1^2\right)\left(1 - t_2^2\right)\left(1 - t_3^2\right)}. \tag{21}$$

If the three A_2 in the initial reducible representation are not distinguished, we can write $t_1 = t_2 = t_3 = t$ in eq 21 to recover eq 17. The same method for $\Gamma^{\mathrm{final}} = A_2$ gives

$$M^{\mathrm{C_i}}\left(A_2; A_2 \oplus A_2 \oplus A_2; t_1, t_2, t_3\right) = \frac{t_1 + t_2 + t_3 + t_1 t_2 t_3}{\left(1 - t_1^2\right)\left(1 - t_2^2\right)\left(1 - t_3^2\right)}, \tag{22}$$

and permits one to recover eq 18.

8. Recursive construction of the integrity bases

Computational algorithms already exist to compute integrity bases[26,52,53], but they are limited to the case where the final representation is totally symmetric. Furthermore, they

are not very efficient for large dimensions. In contrast, the algorithm of section II B 2 that parallels the recursive construction used for the generating functions can be applied to compute efficiently the corresponding integrity basis. Eq 21 contains more information than eq 17, because it allows one to track the origin and the multiplicity of the different terms. For example, the term $(1-t_1^2)$ in the denominator of eq 21 comes from $\frac{1}{1-t_1^2}$ or $\frac{t_1}{1-t_1^2}$. Table II associates the t_1 term in the denominator of these two fractions with the polynomial x_1. As a consequence, x_1^2 belongs to the denominator polynomials of eq 21. The term t_1t_2 on the numerator of eq 21 suggests a product of one numerator of degree one in x_1 and one numerator of degree one in x_2 and leads to the conclusion that the term x_1x_2 belongs to the numerator polynomials of eq 21. The integrity bases for our case example determined with this method are given in Table IV. Remembering that denominator polynomials can be multipled between themselves without any restriction but that numerator polynomials only appear linearly, the lists of invariant and A_2–covariant polynomials of degree k in Table III are straightforwardly computed from the integrity bases in Table IV. The data in Table IV is enough to compute quickly a basis for the vector space of invariant or A_2–covariant polynomials of any degree. For example, the degree 5, A_2–covariant $x_2^2x_3^3 = (x_2^2x_3^2)\cdot x_3$, is the product of a single numerator A_2–covariant, x_3, with the product of denominator invariants $x_2^2x_3^2$.

TABLE IV. Integrity bases for the two generating functions $M^{\mathrm{C_i}}\left(\Gamma^{\mathrm{final}}; A_2\oplus A_2\oplus A_2; t\right)$ involved in the case example.

Γ^{final}	Generating function	Denominator polynomials	Numerator polynomials
A_1	$\frac{1+t_1t_2+t_1t_3+t_2t_3}{(1-t_1^2)(1-t_2^2)(1-t_3^2)}$	$\{x_1^2, x_2^2, x_3^2\}$	$\{1, x_1x_2, x_1x_3, x_2x_3\}$
A_2	$\frac{t_1+t_2+t_3+t_1t_2t_3}{(1-t_1^2)(1-t_2^2)(1-t_3^2)}$	$\{x_1^2, x_2^2, x_3^2\}$	$\{x_1, x_2, x_3, x_1x_2x_3\}$

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,[41] 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 irrep 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 $\Gamma^{\text{initial}} := \mathbb{R} < S_1, S_{2a}, ..., S_{4z} >$ generated by $S_1, S_{2a}, ..., S_{4z}$ over the field of real numbers (to which we restrict ourselves from now on, in view of the applications) splits into a direct sum of irreps:

$$\begin{aligned}\Gamma^{\text{initial}} &= \mathbb{R} < S_1 > \oplus \mathbb{R} < S_{2a}, S_{2b} > \oplus \mathbb{R} < S_{3x}, S_{3y}, S_{3z} > \oplus \mathbb{R} < S_{4x}, S_{4y}, S_{4z} >, \\ &= \Gamma_1^{\text{initial}} \oplus \Gamma_2^{\text{initial}} \oplus \Gamma_3^{\text{initial}} \oplus \Gamma_4^{\text{initial}}. \end{aligned} \tag{23}$$

An extra coordinate S_5 has to be added to map bi–univoquely 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).[17,60] 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^{final}–covariants. The same holds true for S_1. This allows us to reduce the problem to the study of $\mathcal{P}^{\Gamma^{\text{final}}}$, where $\mathcal{P}$ is the polynomial algebra generated by $S_{2a}, S_{2b}, S_{3x}, S_{3y}, S_{3z}, S_{4x}, S_{4y}, S_{4z}$. Note however, that the tabulated integrity bases provided as supplemental material, Appendices A and B, as well as eq 36 correspond to the full 9–dimensional representation Γ^{initial}.

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 $M\left(\Gamma^{\text{final}}; \Gamma_i^{\text{initial}}; t\right)$, where $\Gamma_i^{\text{initial}}$ and Γ^{final} are irreps, are known for O, see ref[58] and Appendix A. The denominator and numerator polynomials of these integrity bases are the building blocks of the construction of the integrity basis for the initial 8–dimensional reducible representation, $\Gamma_0^{\text{initial}} := \mathbb{R} < S_{2a}, S_{2b} > \oplus \mathbb{R} < S_{3x}, S_{3y}, S_{3z} > \oplus \mathbb{R} < S_{4x}, S_{4y}, S_{4z} > = \Gamma_2^{\text{initial}} \oplus \Gamma_3^{\text{initial}} \oplus \Gamma_4^{\text{initial}}$ 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 $\Gamma_0^{\text{initial}}$ 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:

$$f_2 := \frac{S_{2a}^2 + S_{2b}^2}{\sqrt{2}} \tag{24}$$

$$f_3 := \frac{S_{3x}^2 + S_{3y}^2 + S_{3z}^2}{\sqrt{3}} \tag{25}$$

$$f_4 := \frac{S_{4x}^2 + S_{4y}^2 + S_{4z}^2}{\sqrt{3}} \tag{26}$$

2. Degree 3:

$$f_5 := \frac{-S_{2a}^3 + 3S_{2b}^2 S_{2a}}{2} \tag{27}$$

$$f_6 := S_{3x} S_{3y} S_{3z} \tag{28}$$

$$f_7 := S_{4x} S_{4y} S_{4z} \tag{29}$$

3. Degree 4:

$$f_8 := \frac{S_{3x}^4 + S_{3y}^4 + S_{3z}^4}{\sqrt{3}} \tag{30}$$

$$f_9 := \frac{S_{4x}^4 + S_{4y}^4 + S_{4z}^4}{\sqrt{3}} \ . \tag{31}$$

B. Numerator polynomials of the integrity bases

The Molien series for the action of T_d on $\Gamma_0^{\text{initial}}$ can be directly computed using Burnside's generalization[59] of the Molien's results.[57] However, as suggested by the case example with $\mathrm{C_i}$ symmetry, it is computationally more efficient to use eq 5 to recursively construct the Molien generating functions and the integrity bases. Setting $G = \mathrm{T}_d$, a non–zero $c^{\Gamma}_{\Gamma_\alpha, \Gamma_\beta}$

coefficient in the sum of eq 5 relates at each step of the recursive algorithm to a possible non–zero numerator Γ_f–covariant in the integrity basis of the generating function $M^{\mathrm{T}_d}\left(\Gamma^{\text{final}}; \Gamma_1^{\text{initial}} \oplus \Gamma_2^{\text{initial}} \oplus \Gamma_3^{\text{initial}} \oplus \Gamma_4^{\text{initial}}; t_1, t_2, t_3, t_4\right)$. The corresponding polynomial is built by coupling previously obtained polynomials with Clebsch–Gordan coefficients of the group T_d.[12]

As an example, let us compute $M^{\mathrm{T}_d}\left(E; F_2 \oplus F_2; t_3, t_4\right)$. The product table of the irreps of the group T_d is given in Table V. We can construct objects that transform according to any of the five irreps from objects that carry the F_2 irrep. As a consequence, the five $M^{\mathrm{T}_d}\left(\Gamma_\alpha; F_2; t\right)$, with Γ_α an irrep, are non–zero. Table V indicates that the direct product $\Gamma_\alpha \times \Gamma_\beta$ contains the E representation if and only if the pair $(\Gamma_\alpha, \Gamma_\beta)$ belongs to the following set:

$$\left\{(A_1, E), (E, A_1), (A_2, E), (E, A_2), (E, E), (F_1, F_1), (F_1, F_2), (F_2, F_1), (F_2, F_2)\right\}. \quad (32)$$

TABLE V. Product table of the irreps of the group T_d.

	A_1	A_2	E	F_1	F_2
A_1	A_1	A_2	E	F_1	F_2
A_2	A_2	A_1	E	F_2	F_1
E	E	E	$A_1 \oplus A_2 \oplus E$	$F_1 \oplus F_2$	$F_1 \oplus F_2$
F_1	F_1	F_2	$F_1 \oplus F_2$	$A_1 \oplus E \oplus F_1 \oplus F_2$	$A_2 \oplus E \oplus F_1 \oplus F_2$
F_2	F_2	F_1	$F_1 \oplus F_2$	$A_2 \oplus E \oplus F_1 \oplus F_2$	$A_1 \oplus E \oplus F_1 \oplus F_2$

According to eq 5, each of the nine pairs $(\Gamma_\alpha, \Gamma_\beta)$ of eq 32 contributes to a term in the expansion

$$M^{\mathrm{T}_d}\left(E; F_2 \oplus F_2; t_3, t_4\right) = \sum_{\Gamma_\alpha, \Gamma_\beta} c^E_{\Gamma_\alpha, \Gamma_\beta} M^{\mathrm{T}_d}\left(\Gamma_\alpha; F_2; t_3\right) M^{\mathrm{T}_d}\left(\Gamma_\beta; F_2; t_4\right). \quad (33)$$

The expressions of the elementary generating functions $M^{\mathrm{T}_d}\left(\Gamma; F_2; t\right)$ are given in ref[58] and Appendix A. As an example, the pair (F_2, F_1) of eq 32 will give the following contribution in eq 33:

$$c^E_{F_2, F_1} M^{\mathrm{T}_d}\left(F_2; F_2; t_3\right) M^{\mathrm{T}_d}\left(F_1; F_2; t_4\right) = \frac{\left(t_3 + t_3^2 + t_3^3\right)\left(t_4^3 + t_4^4 + t_4^5\right)}{\left(1 - t_3^2\right)\left(1 - t_3^3\right)\left(1 - t_3^4\right)\left(1 - t_4^2\right)\left(1 - t_4^3\right)\left(1 - t_4^4\right)}. \quad (34)$$

The interpretation of the right–hand side of eq 34 in terms of integrity basis suggests that the pair (F_2, F_1) of eq 32 will contribute to 6 denominators and $2\times 9 = 18$ numerator polynomials to the integrity basis of $M^{\mathrm{T}_d}(E; F_2 \oplus F_2; t_3, t_4)$. The 6 denominator polynomials are simply the union of the set of the denominator invariants associated to the $M^{\mathrm{T}_d}(F_2; F_2; t_3)$ and $M^{\mathrm{T}_d}(F_1; F_2; t_4)$ elementary generating functions. Each product $t_3^{n_3} t_4^{n_4}$ in the numerator of eq 34 corresponds to a numerator polynomial of symmetry E, i obtained by coupling via the Clebsch–Gordan coefficients of the T_d group the numerator polynomial of symmetry F_2, j, degree n_3 that belongs to the integrity basis of $M^{\mathrm{T}_d}(F_2; F_2; t_3)$ with the numerator polynomial of symmetry F_1, k, degree n_4 that belongs to the integrity basis of $M^{\mathrm{T}_d}(F_1; F_2; t_4)$. The expansion of the product $(t_3 + t_3^2 + t_3^3)(t_4^3 + t_4^4 + t_4^5)$ contains 9 terms and each term contributes to two polynomials, one of symmetry type E, a and the other of symmetry type E, b, hence the $2 \times 9 = 18$ numerator polynomials.

This recursive algorithm has the advantage that only the integrity bases for initial irreps, see Appendix A, and the Clebsch–Gordan coefficients of the group T_d 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}. The fully coupled generating function for the F_2 final irrep reads:

$$M^{\mathrm{T}_d}\left(F_2; \Gamma_0^{\mathrm{initial}}; t\right) = \frac{\mathcal{N}\left(F_2; \Gamma_0^{\mathrm{initial}}; t\right)}{(1-t^2)^3(1-t^3)^3(1-t^4)^2}, \tag{35}$$

with

$$\begin{aligned}
&\mathcal{N}\left(F_2; \Gamma_0^{\mathrm{initial}}; t\right) \\
&= 2t + 5t^2 + 12t^3 + 23t^4 + 41t^5 + 60t^6 + 71t^7 + 71t^8 \\
&\quad +60t^9 + 45t^{10} + 27t^{11} + 12t^{12} + 3t^{13}.
\end{aligned} \tag{36}$$

Finally, to deal with the coordinate S_1, it suffices to note that

$$M^{\mathrm{T}_d}\left(F_2; \Gamma^{\mathrm{initial}}; t\right) = \frac{M^{\mathrm{T}_d}\left(F_2; \Gamma_0^{\mathrm{initial}}; t\right)}{(1-t)}. \tag{37}$$

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

As far as the F_2 representation is concerned, Table VI tells that there are 432 numerator polynomials of symmetry type F_2, z: $\left\{g_1^{F_2,z}, ..., g_{432}^{F_2,z}\right\}$ of which 2 are of degree one, 5 of degree two, 12 of degree three, and so on. We finally obtain that an arbitrary polynomial of

TABLE VI. Numbers $n_k^{\Gamma^{\rm final}}$ of $\Gamma^{\rm final}$–covariant numerator polynomials of degree k and dimensions $\dim \mathcal{P}_k^{\Gamma^{\rm final},i}$, $1 \leq i \leq \left[\Gamma^{\rm final}\right]$, of the vector spaces $\mathcal{P}_k^{\Gamma^{\rm final},i}$ of covariant polynomials of type $\Gamma^{\rm final}, i$ and of degree k, $\Gamma^{\rm final} \in \{A_1, A_2, E, F_1, F_2\}$. The total number $\sum_{k=0}^{15} n_k^{\Gamma^{\rm final}}$ of $\Gamma^{\rm final}$–covariant numerator polynomials is equal to $\left[\Gamma^{\rm final}\right] \times \Pi_j d_j/|G|$, where $\left[\Gamma^{\rm final}\right]$ is the dimension of the irrep $\Gamma^{\rm final}$, $|G| = 24$ 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[26]. 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 $\left[\Gamma^{\rm final}\right]$ for $\pi = Id$, see also Proposition 4.9 of ref[56].

$\Gamma^{\rm final}$:	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	∞

symmetry type F_2, m, $m \in \{x, y, z\}$ in the algebra spanned by the $S_1, \ldots, S_{4z}$ coordinates

will identify with a unique linear combination of monomials:

$$f_1^{j_1} f_2^{j_2} ... f_9^{j_9} g_k^{F_2,m} \quad (j_1, \ldots j_9) \in \mathbb{N}^9, \ 1 \leq k \leq 432. \tag{38}$$

The lists of numerator polynomials for all irreps are provided as supplemental material.[54] They have been derived in a few seconds of CPU time on a laptop by using the MAPLE computer algebra system.[61] 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 recipe is given in Appendix B. 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 Γ^{initial}, see Table VI and compare with ref[7] where 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.[15,45] There are 1998 linearly independent invariants of degree 10 for representation Γ^{initial}. 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.[50,62] The 9 basic invariants and 143 F_2, z-covariant numerator polynomials of degree less or equal to 6 (see Table VI) 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

Our recursive method for constructing invariants and covariants blends ideas from the theory of invariants and from techniques used in applications of group theory to physics and chemistry. We have determined for the first time integrity bases of the Γ^{final}–covariants of the group T_d acting on the 9 (or possibly 10) symmetrized internal coordinates of a XY_4 molecule. They are composed of nine algebraically independent denominator polynomials and a finite number of Γ^{final}–covariant numerator polynomials given in the supplemental material.[54]

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, (and used in many studies of methane PES or EDMS as recalled in introduction), to construct an integrity basis for each final representation Γ^{final}. Integrity basis sets are first determined for each single, possibly degenerate, irrep 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^{final}–covariants is general since the Γ^{final}–covariant polynomials admit a Hironaka decomposition[56] for any finite group G. Any "internal coordinate system" (coordinates for internal degrees of freedom) $(q_i)_i$, or internal displacement coordinates $(q_i - q_i^0)_i$, with respect to a molecular reference configuration $(q_i^0)_i$ totally invariant under G, can be symmetrized to obtain symmetry-adapted coordinates. Polynomials in the latter coordinates can in turn be used to represent PES and other functions of nuclear geometries. This is straightforward when such a function is independent of the orientational coordinates (e.g. Euler angles) of the moving axes, like the PES, or the EDMS in the body-frame when using O(3)-invariant coordinates: the moving–frame–dependent part being then all included in the direction–cosines which relate the EDM in the body-frame to the EDM in the laboratory-frame. However, for pentatomic and beyond the use of O(3)-invariant coordinates necessarily implies auxiliary coordinates (such as S_5 in the case treated here) to cover the full configuration space[63] and one may wish to employ moving-frame-dependent symmetry coordinates instead. Then, our approach can be useful to obtain covariant bases of the permutation-invariant group, however, the total symmetry group acting on the $3N-3$ (orientational + shape) coordinates is only a semi-direct product of the permutation-inversion group by SO(3) which makes the exploitation of symmetry for the EDMS in the laboratory-frame more involved. The problem of body-frame definition and singularities[64] is out of the scope of the present paper.

So, in many cases of chemical interest, 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,[51] which go far beyond the classical Molien series approach in quantum chemistry.

Last but not least, 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 can be generated by simple multiplications between polynomials in the integrity bases of this paper in a direct manner as illustrated in Appendix B.

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Appendix A: 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 irrep E is doubly degenerate, while the F_1 and F_2 irreps are triply degenerate. The procedure detailed in section II is based on the knowledge of the generating functions $M^{\mathrm{T}_d}\left(\Gamma^{\mathrm{final}};\Gamma^{\mathrm{initial}};t\right)$, where $\Gamma^{\mathrm{initial}}$ and Γ^{final} are irreps of the group T_d. The coefficient c_n in the Taylor expansion $c_0 + c_1 t + c_2 t^2 + \cdots$ of the generating function gives the number of linearly independent Γ^{final}–covariant polynomials of degree n that can be constructed from the objects in the initial $\Gamma^{\mathrm{initial}}$ representation.

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

$$M^{\mathrm{T}_d}\left(\Gamma^{\mathrm{final}};\Gamma^{\mathrm{initial}};t\right) = \frac{\mathcal{N}\left(\Gamma^{\mathrm{final}};\Gamma^{\mathrm{initial}};t\right)}{\mathcal{D}\left(\Gamma^{\mathrm{initial}};t\right)} = \frac{\sum\limits_{k=1}^{N} t^{\nu_k}}{\prod\limits_{k=1}^{D}\left(1-t^{\delta_k}\right)}, \tag{A1}$$

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 $I^{(\delta_k)}\left(\Gamma^{\mathrm{initial}}\right)$. The polynomial associated to a t^{ν_k} term in the numerator is a Γ^{final}–covariant called a numerator polynomial of degree ν_k and is noted $E^{(\nu_k)}\left(\Gamma^{\mathrm{final}};\Gamma^{\mathrm{initial}}\right)$ (when Γ^{final} is degenerate, $E^{(\nu_k)}\left(\Gamma^{\mathrm{final}};\Gamma^{\mathrm{initial}}\right)$ will be a vector gathering all the $\Gamma^{\mathrm{final}}, i$–covariant numerator

polynomials of degree ν_k for $i \in \{1, \ldots, \left[\Gamma^{\text{final}}\right]\}$). According to the expression, eq A1, D denominator polynomials and N numerator polynomials are associated to the generating function, $M^{\mathrm{T}_d}\left(\Gamma^{\text{final}}; \Gamma^{\text{initial}}; t\right)$.

We will closely follow the article of Patera, Sharp and Winternitz[58] for the notation for denominator and numerator polynomials, using α, β, γ symbols for a chosen basis of each irrep. However, their table for octahedral tensors contains two errors for the degree eight $E^{(8)}\left(\Gamma_4; \Gamma_4\right)$ and degree seven $E^{(7)}\left(\Gamma_5; \Gamma_4\right)$ numerator polynomials. With the definitions of polynomials given in ref[58], the following relation hold:

$$\begin{aligned} E^{(8)}\left(\Gamma_4; \Gamma_4\right)_i = & I^{(2)}\left(\Gamma_4\right) E^{(6)}\left(\Gamma_4; \Gamma_4\right)_i \\ & -\frac{1}{2} I^{(2)}\left(\Gamma_4\right)^2 E^{(4)}\left(\Gamma_4; \Gamma_4\right)_i \\ & +\frac{1}{2} I^{(4)}\left(\Gamma_4\right) E^{(4)}\left(\Gamma_4; \Gamma_4\right)_i , \end{aligned} \tag{A2}$$

where the index i stands either for x, y or z. The relation eq A2 indicates that the polynomial of degree eight $E^{(8)}\left(\Gamma_4; \Gamma_4\right)$ has a decomposition in terms of polynomials that are elements of the integrity basis associated to $M^{\mathrm{T}_d}\left(\Gamma_4; \Gamma_4; t\right)$. As a consequence, $E^{(8)}\left(\Gamma_4; \Gamma_4\right)$ does not enter the integrity basis.

The same is true for $E^{(7)}\left(\Gamma_5; \Gamma_4\right)$ and the integrity basis associated to $M^{\mathrm{T}_d}\left(\Gamma_5; \Gamma_4; t\right)$ due to following relation:

$$\begin{aligned} E^{(7)}\left(\Gamma_5; \Gamma_4\right)_i = & I^{(2)}\left(\Gamma_4\right) E^{(5)}\left(\Gamma_5; \Gamma_4\right)_i \\ & -\frac{1}{2} I^{(2)}\left(\Gamma_4\right)^2 E^{(3)}\left(\Gamma_5; \Gamma_4\right)_i \\ & +\frac{1}{2} I^{(4)}\left(\Gamma_4\right) E^{(3)}\left(\Gamma_5; \Gamma_4\right)_i . \end{aligned} \tag{A3}$$

A complete list of tables of both denominator and numerator polynomials for all the initial Γ^{initial} and final Γ^{final} irreps is given in the next sections.

1. $\Gamma^{\text{initial}} = A_1$ irreducible representation

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

2. $\Gamma^{\text{initial}} = A_2$ **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. $\Gamma^{\text{initial}} = E$ **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

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

4. $\Gamma^{\text{initial}} = F_1$ **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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

5. $\Gamma^{\text{initial}}=F_2$ irreducible representation

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

$t^3+t^4+t^5$, 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

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

Appendix B: Application of the integrity base for F_2–covariant polynomials: Representation of the electric dipole moment surface of a tetrahedral XY_4 molecule

1. Introduction

Appendix B gives an application of the integrity basis for F_2–covariant polynomials of tetrahedral XY_4 molecules. The integrity basis determined in this paper contains the denominator polynomials f_i, $1 \leq i \leq 9$, listed in the main text and the auxiliary numerators published in the file `symmetries_A1_A2_E_F1_F2.txt` available as supplemental material.[54] This example can be transposed to any other final irrep Γ^{final}.

The electric dipole moment surface of a tetrahedral XY_4 molecule can be built as a linear combination of F_2–covariant polynomials of total degree less than $d_{\max}$ in the coordinates that span the representation, Γ^{initial}, of eq 23. The integer $d_{\max}$ is the order of the expansion. The generating function for the number of F_2–covariant polynomials built from this representation reads (see eqs 35 to 37):

$$\frac{2t + 5t^2 + 12t^3 + 23t^4 + 41t^5 + 60t^6 + 71t^7 + 71t^8 + 60t^9 + 45t^{10} + 27t^{11} + 12t^{12} + 3t^{13}}{(1-t)\left(1-t^2\right)^3\left(1-t^3\right)^3\left(1-t^4\right)^2},$$

whose Taylor expansion up to order four is given by:

$$2t + 7t^2 + 25t^3 + 69t^4 + \cdots. \tag{B1}$$

The coefficients in eq B1 mean that there are 2 (respectively 7, 25, and 69) linearly independent F_2, α–covariant polynomials of degree one (respectively two, three, and four), $\alpha \in \{x, y, z\}$. We now detail the construction of these 103 F_2, x polynomials. The F_2, y and F_2, z polynomials may be built using the same procedure.

The expansion of the F_2, x-EDMS up to order four is a linear combination of 103 F_2, x–polynomials:

$$\begin{aligned}&\mu_{F_2,x}\left(S_1, S_{2a}, S_{2b}, S_{3x}, S_{3y}, S_{3z}, S_{4x}, S_{4y}, S_{4z}\right)\\ &= \sum_{i=1}^{103} c_i^{F_2,x} \times p_i^{F_2,x}\left(S_1, S_{2a}, S_{2b}, S_{3x}, S_{3y}, S_{3z}, S_{4x}, S_{4y}, S_{4z}\right).\end{aligned} \tag{B2}$$

The coefficients $c_i^{F_2,x}$ of eq B2 are to be determined by fitting the expression to either experimental or *ab initio* data. We know that the 103, F_2, x–polynomials, $p_i^{F_2,x}$, can be

written as a product of denominator polynomials powered to any positive integer value, and a single numerator polynomial. So, the polynomials that enter the expansion of the F_2, x component of the EDMS can all be taken of the form:

$$\varphi_{k,l}^{F_2,x} \times f_1^{n_1} f_2^{n_2} \cdots f_9^{n_9}, \tag{B3}$$

where the $(\varphi_{k,l}^{F_2,x})_{1 \leq l \leq n_k^{F_2}}$ denotes the numerator polynomials of degree k, (we change the notation with respect to the main text to include explicitly the degree k). Their numbers, $n_k^{F_2}$, are given in the column labelled F_2 of Table VI. Sets of linearly independent $p_i^{F_2,x}$ are listed below by degrees. We recall that f_1 is a polynomial of degree one, f_2, f_3, and f_4 are three polynomials of degree two, f_5, f_6, and f_7 are three polynomials of degree three, and f_8, f_9 are two polynomials of degree four.

2. Degree one

The 2 F_2, x linearly independent polynomials of total degree one compatible with eq B3 are $p_1^{F_2,x} = \varphi_{1,1}^{F_2,x}$ and $p_2^{F_2,x} = \varphi_{1,2}^{F_2,x}$.

3. Degree two

The 7 F_2, x linearly independent polynomials of total degree two compatible with eq B3 are:

$$\begin{aligned} &p_3^{F_2,x} = \varphi_{2,1}^{F_2,x}, \quad p_4^{F_2,x} = \varphi_{2,2}^{F_2,x}, \quad p_5^{F_2,x} = \varphi_{2,3}^{F_2,x}, \; p_6^{F_2,x} = \varphi_{2,4}^{F_2,x}, \; p_7^{F_2,x} = \varphi_{2,5}^{F_2,x}, \\ &p_8^{F_2,x} = \varphi_{1,1}^{F_2,x} f_1, \; p_9^{F_2,x} = \varphi_{1,2}^{F_2,x} f_1. \end{aligned}$$

4. Degree three

The 25 F_2, x linearly independent polynomials of total degree three compatible with eq B3 are:

$$\begin{aligned} &p_{10}^{F_2,x} = \varphi_{3,1}^{F_2,x}, \quad p_{11}^{F_2,x} = \varphi_{3,2}^{F_2,x}, \quad p_{12}^{F_2,x} = \varphi_{3,3}^{F_2,x}, \quad p_{13}^{F_2,x} = \varphi_{3,4}^{F_2,x}, \quad p_{14}^{F_2,x} = \varphi_{3,5}^{F_2,x}, \\ &p_{15}^{F_2,x} = \varphi_{3,6}^{F_2,x}, \quad p_{16}^{F_2,x} = \varphi_{3,7}^{F_2,x}, \quad p_{17}^{F_2,x} = \varphi_{3,8}^{F_2,x}, \quad p_{18}^{F_2,x} = \varphi_{3,9}^{F_2,x}, \quad p_{19}^{F_2,x} = \varphi_{3,10}^{F_2,x}, \\ &p_{20}^{F_2,x} = \varphi_{3,11}^{F_2,x}, \quad p_{21}^{F_2,x} = \varphi_{3,12}^{F_2,x}, \quad p_{22}^{F_2,x} = \varphi_{2,1}^{F_2,x} f_1, \; p_{23}^{F_2,x} = \varphi_{2,2}^{F_2,x} f_1, \; p_{24}^{F_2,x} = \varphi_{2,3}^{F_2,x} f_1, \\ &p_{25}^{F_2,x} = \varphi_{2,4}^{F_2,x} f_1, \; p_{26}^{F_2,x} = \varphi_{2,5}^{F_2,x} f_1, \; p_{27}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_1^2, \; p_{28}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_1^2, \; p_{29}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_2, \\ &p_{30}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_2, \; p_{31}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_3, \; p_{32}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_3, \; p_{33}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_4, \; p_{34}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_4. \end{aligned}$$

5. Degree four

The 69 F_2, x linearly independent polynomials of total degree four compatible with eq B3 are:

$$
\begin{array}{lllll}
p_{35}^{F_2,x} = \varphi_{4,1}^{F_2,x}, & p_{36}^{F_2,x} = \varphi_{4,2}^{F_2,x}, & p_{37}^{F_2,x} = \varphi_{4,3}^{F_2,x}, & p_{38}^{F_2,x} = \varphi_{4,4}^{F_2,x}, & p_{39}^{F_2,x} = \varphi_{4,5}^{F_2,x}, \\
p_{40}^{F_2,x} = \varphi_{4,6}^{F_2,x}, & p_{41}^{F_2,x} = \varphi_{4,7}^{F_2,x}, & p_{42}^{F_2,x} = \varphi_{4,8}^{F_2,x}, & p_{43}^{F_2,x} = \varphi_{4,9}^{F_2,x}, & p_{44}^{F_2,x} = \varphi_{4,10}^{F_2,x}, \\
p_{45}^{F_2,x} = \varphi_{4,11}^{F_2,x}, & p_{46}^{F_2,x} = \varphi_{4,12}^{F_2,x}, & p_{47}^{F_2,x} = \varphi_{4,13}^{F_2,x}, & p_{48}^{F_2,x} = \varphi_{4,14}^{F_2,x}, & p_{49}^{F_2,x} = \varphi_{4,15}^{F_2,x}, \\
p_{50}^{F_2,x} = \varphi_{4,16}^{F_2,x}, & p_{51}^{F_2,x} = \varphi_{4,17}^{F_2,x}, & p_{52}^{F_2,x} = \varphi_{4,18}^{F_2,x}, & p_{53}^{F_2,x} = \varphi_{4,19}^{F_2,x}, & p_{54}^{F_2,x} = \varphi_{4,20}^{F_2,x}, \\
p_{55}^{F_2,x} = \varphi_{4,21}^{F_2,x}, & p_{56}^{F_2,x} = \varphi_{4,22}^{F_2,x}, & p_{57}^{F_2,x} = \varphi_{4,23}^{F_2,x}, & p_{58}^{F_2,x} = \varphi_{2,1}^{F_2,x} f_2, & p_{59}^{F_2,x} = \varphi_{2,2}^{F_2,x} f_2, \\
p_{60}^{F_2,x} = \varphi_{2,3}^{F_2,x} f_2, & p_{61}^{F_2,x} = \varphi_{2,4}^{F_2,x} f_2, & p_{62}^{F_2,x} = \varphi_{2,5}^{F_2,x} f_2, & p_{63}^{F_2,x} = \varphi_{2,1}^{F_2,x} f_3, & p_{64}^{F_2,x} = \varphi_{2,2}^{F_2,x} f_3, \\
p_{65}^{F_2,x} = \varphi_{2,3}^{F_2,x} f_3, & p_{66}^{F_2,x} = \varphi_{2,4}^{F_2,x} f_3, & p_{67}^{F_2,x} = \varphi_{2,5}^{F_2,x} f_3, & p_{68}^{F_2,x} = \varphi_{2,1}^{F_2,x} f_5, & p_{69}^{F_2,x} = \varphi_{2,2}^{F_2,x} f_5, \\
p_{70}^{F_2,x} = \varphi_{2,3}^{F_2,x} f_5, & p_{71}^{F_2,x} = \varphi_{2,4}^{F_2,x} f_5, & p_{72}^{F_2,x} = \varphi_{2,5}^{F_2,x} f_5, & p_{73}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_5, & p_{74}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_5, \\
p_{75}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_6, & p_{76}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_6, & p_{77}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_7, & p_{78}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_7, & p_{79}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_1 f_2, \\
p_{80}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_1 f_2, & p_{81}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_1 f_3, & p_{82}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_1 f_3, & p_{83}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_1 f_4, & p_{84}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_1 f_4, \\
p_{85}^{F_2,x} = \varphi_{3,1}^{F_2,x} f_1, & p_{86}^{F_2,x} = \varphi_{3,2}^{F_2,x} f_1, & p_{87}^{F_2,x} = \varphi_{3,3}^{F_2,x} f_1, & p_{88}^{F_2,x} = \varphi_{3,4}^{F_2,x} f_1, & p_{89}^{F_2,x} = \varphi_{3,5}^{F_2,x} f_1, \\
p_{90}^{F_2,x} = \varphi_{3,6}^{F_2,x} f_1, & p_{91}^{F_2,x} = \varphi_{3,7}^{F_2,x} f_1, & p_{92}^{F_2,x} = \varphi_{3,8}^{F_2,x} f_1, & p_{93}^{F_2,x} = \varphi_{3,9}^{F_2,x} f_1, & p_{94}^{F_2,x} = \varphi_{3,10}^{F_2,x} f_1, \\
p_{95}^{F_2,x} = \varphi_{3,11}^{F_2,x} f_1, & p_{96}^{F_2,x} = \varphi_{3,12}^{F_2,x} f_1, & p_{97}^{F_2,x} = \varphi_{2,1}^{F_2,x} f_1^2, & p_{98}^{F_2,x} = \varphi_{2,2}^{F_2,x} f_1^2, & p_{99}^{F_2,x} = \varphi_{2,3}^{F_2,x} f_1^2, \\
p_{100}^{F_2,x} = \varphi_{2,4}^{F_2,x} f_1^2, & p_{101}^{F_2,x} = \varphi_{2,5}^{F_2,x} f_1^2, & p_{102}^{F_2,x} = \varphi_{1,1}^{F_2,x} f_1^3, & p_{103}^{F_2,x} = \varphi_{1,2}^{F_2,x} f_1^3. &
\end{array}
$$

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