Symmetry-Adapted Polynomial Basis for Global Potential Energy Surfaces - Applications to XY_4 Molecules.

Mathematical methods for *ab initio* quantum chemistry.

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- It is often necessary to deal with potential energy surfaces (P.E.S.) in a large domain of the nuclear configuration space.
- Spectroscopy: case of floppy systems and/or highly-excited states
- Chemical reaction dynamics, dissociation paths.
- Here, we will concentrate on the example of CH_4 with a view to spectroscopy.
- Results on polynomial fitting of global P.E.S. are valid in full generality and extend to the case where the polynomial is in factor of an arbitrary totally symmetric function.

Taking advantage of the permutation-translation-rotation-inversion (PTRI) group.

- The electronic potential energy surfaces for the nuclei (P.E.S.) used in quantum chemistry inherit the symmetry of the whole molecular system.
- Some PTRI invariance properties can be easily incorporated in a *local* description of the P.E.S. (eg by choosing symmetry-adapted local coordinates).

  They *can not*, on structural grounds, be easilly incorporated in a global description, due to invariant theory phenomena (more later).

Goal of the talk.

- The present work presents a simplified technique to obtain symmetry-adapted polynomial basis for global PES, together with algorithmic recipes that make the problem computationnally tractable.
- It is the prolongation of the works of Schmelzer and Murrell (Int. J. Quantum Chemistry, 1985) and of Collins and Parsons (J. Chem. Phys., 1993) on the subject.

Historical background

- The introduction of the theory of algebraic invariants to expand a PES can be traced back to the work of Schmelzer and Murrell (Int. J. Quantum Chemistry, 1985).
- They studied finite molecular point group actions to obtain the dimensions of basis made of homogeneous invariant polynomials in the internal coordinates.
- Since, given a linear representation of a (finite or, more generally, compact) group G, all smooth G-invariant functions are smooth functions of invariant polynomials (Schwarz, 1975), this approach is suitable to express any polynomial, analytic or C^∞ invariant functions.

- However, the study of *invariant polynomials in the local coordinates under the nuclear permutation group* is not enough if the goal is the study of a large domain of the configuration space.
- The reason is classical: even without considering invariants, it is well known that local coordinates do not determine the shape of a molecule -and one has usually to add extra, "redundant" coordinates to specify the shape.

E.g. CH_4: Wang-Carrington, J. Chem. Phys. (2003).
They consider the bend symmetry coordinates for methane

$$s_a = \frac{1}{\sqrt{12}}(2\omega_{12} - \omega_{13} - \omega_{14} - \omega_{23} - \omega_{24} + 2\omega_{34}),$$

$$s_b = \frac{1}{2}(\omega_{13} - \omega_{14} - \omega_{23} + \omega_{24}),$$

$$s_x = \frac{1}{\sqrt{2}}(\omega_{24} - \omega_{13}),\ s_y = \frac{1}{\sqrt{2}}(\omega_{23} - \omega_{14}),\ s_z = \frac{1}{\sqrt{2}}(\omega_{34} - \omega_{12}),$$

$$\omega_{ij} = \cos\alpha_{ij},$$

where α_{ij} is the angle between bond vectors i and j.
The lengths of the four bond vectors and the bend symmetry coordinates do not determine the shape of the molecule. They show that there are actually either one or two physical possible shapes.

- The ambiguities can be removed by adding an extra symmetry coordinate.
- Wang and Carrington also suggest a rule to choose a unique shape for given values of the bend coordinates, but *"such a rule entails excluding shapes and therefore cannot be used to calculate high-lying levels"*.
- These restrictions also apply to the approach by Schmelzer and Murrell.

- The Schmelzer-Murrell approach was extended by Collins and Parsons to include the rotation-inversion group action in the picture.
- Idea: generalize to the permutation-translation-rotation-inversion group the classical constructions of $O(3)$ and finite group invariants.
- Fundamental tool: the Molien series associated to the linear action of a compact Lie group G. The series can be computed as:

$$\Phi(\lambda) = \int_G \frac{1}{det[I - \lambda M(\beta)]} d\mu(\beta),$$

  where μ is the Haar mesure on G
- Problem: in practice, the approach is restricted to molecules with small permutation group.

Two simple ideas behind the recursive procedure to be introduced:

1. Treat separately (desentangle, at the invariant level), the action of the orthogonal group and the one of the nuclear permutation group.
2. Take systematically advantage of modern invariant theory (Cohen-MacCauley rings in particular) to reformulate and handle the problem.

First step: symmetry-adaptation to the rotation-inversion group $O(3)$.

- Recall that, for a molecule with N atoms, the P.E.S. is (except in a domain of measure zero) a $(3N-6)$-manifold.
- Locally, one may therefore choose a paramerization of the surface by $3N-6$ local coordinates. However, as we have seen with CH_4, for molecules containing five atoms or more, the same values taken by the set of $3N-6$ coordinates can correspond to several physically inequivalent geometries.

- So, one or several, “redundant” coordinates have to be added to the “basic” ones in order to get a one-to-one correspondance between sets of coordinates and molecular shapes.
- Of course, for dimensional reasons, the redundant coordinates must be constrained to satisfy algebraic equations (called *syzygies* in the language of ring theory) relating them to the $(3N - 6)$ basic, free coordinates.
- The fundamental reason for this need of redundant coordinates is explained by a classical result due to Weyl.

- Weyl's second main theorem for the orthogonal group (*The classical groups*, 1946) shows that the natural choice of, possibly redundant, $O(3)$-invariant coordinates, is the set of the $\frac{N(N-1)}{2}$ scalar products of $(N-1)$ "internal" vectors.
- So, the algebra of $O(3)$-invariant polynomials in the Cartesians coordinates, $\mathcal{P}$, is the algebra spanned by exactly $\frac{N(N-1)}{2}$ polynomial invariant of degree 2.
- Out of this minimal set of $\frac{N(N-1)}{2}$ generators, one is free to form (by linear combination) $(3N-6)$ basic, algebraically independent coordinates and $\frac{N(N-1)}{2} - (3N-6) = \frac{N^2-7N+12}{2}$ auxiliary invariant coordinates, related to the basic ones through (explicit) syzygies.

- As a corollary of Weyl's computations, one gets a precise picture of the algebra of $O(3)$-invariant polynomials.
- Let us once again exemplify with the particular case of the methane molecule.
- For this molecule, we take for body-fixed origin the Radau origin X. The Radau vectors $\overrightarrow{XH_i}$ corresponding to hydrogen nuclei positions, are written $\overrightarrow{r}_i = (x_i^1, x_i^2, x_i^3), i = 1, ..., 4$
- We follow Weyl and define $10 = \frac{N(N-1)}{2}$, $N = 5$ $O(3)$-invariant coordinates by setting,

$$d_{i,j} := \langle \overrightarrow{r_i} | \overrightarrow{r_j} \rangle \ .$$

We further ask that the coordinates be adapted to the Σ_4 nuclear permutation symmetry of the molecule, and choose the following $9 = 12 - 3 = 12 - dimO(3)$ basic coordinates:

$$S_1 := \frac{1}{2}(d_{11} + d_{22} + d_{33} + d_{44})$$

$$S_{2a} := \frac{1}{\sqrt{12}}(2d_{12} - d_{13} - d_{14} - d_{23} - d_{24} + 2d_{34})$$

$$S_{2b} := \frac{1}{2}(d_{13} - d_{14} - d_{23} + d_{24}), S_{3x} := \frac{1}{2}(d_{11} - d_{22} + d_{33} - d_{44})$$

$$S_{3y} := \frac{1}{2}(d_{11} - d_{22} - d_{33} + d_{44}), S_{3z} := \frac{1}{2}(d_{11} + d_{22} - d_{33} - d_{44})$$

$$S_{4x} := \frac{1}{\sqrt{2}}(d_{24} - d_{13}), S_{4y} := \frac{1}{\sqrt{2}}(d_{23} - d_{14})$$

$$S_{4z} := \frac{1}{\sqrt{2}}(d_{34} - d_{12}).$$

These are essentially the usual symmetry-adapted linear combinations used in many studies on XY_4 molecules (eg in Wang-Carrington), but here, they are linear combinations of the $d_{i,j}$ instead of bond lengths and bond angles or cosines of bond angles. As a consequence of Weyl's result, since $N = 5$, one has to introduce an extra (or *redundant*) symmetry coordinate, to make the system complete. For example,

$$S_5 := \frac{1}{\sqrt{6}}(d_{12} + d_{13} + d_{14} + d_{23} + d_{24} + d_{34}),$$

S_5 being the solution of a unique, monic, quartic, polynomial syzygy:

$$X^4 + \alpha_3 X^3 + \alpha_2 X^2 + \alpha_1 X + \alpha_0,$$

where α_i is a homogeneous polynomial of degree $4 - i$ into the remaining coordinates S_1, ..., S_{4z}.

This property implies that any $O(3)$-invariant polynomial P in the Cartesians can be written uniquely 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 algebraically free variables $S_1, ..., S_{4z}$.

Conclusion: The algebra $\mathcal{P}$ of invariant polynomials under the action of the rotation-inversion group is, whenever $N \geq 5$, a free module over a polynomial algebra (generated by $3N - 6$ degree 2 polynomials in the cartesian coordinates).

Next step: symmetry-adaptation to the nuclear permutation group.

Interlude: Cohen-Macaulay algebras

- Weyl's algebras of $O(3)$-invariants are a particular case of Cohen-Macaulay algebras -which appear to be the right framework to reformulate problems of invariant computations for the molecular symmetry groups.
- Recall a few facts and definitions.
- *Definition 1: Let A be a graded algebra (eg over the real numbers -say $\mathcal{P}$). The Krull dimension m of A is the maximal number of algebraically independent elements in A (eg $3N-6$).*
- *Definition 2: A set $\theta_1, ..., \theta_m$ of m homogeneous elements of positive degree is a homogeneous system of parameters (hsop) if A is a finitely generated module over the polynomial algebra $\mathbf{C}[\theta_1, ..., \theta_m]$.*

- *The algebra A is Cohen-Macaulay* if A is a free module over $\mathbf{C}[\theta_1, ..., \theta_m]$ (eg $\mathcal{P}$ is a free module over the polynomial algebra generated by the basic coordinates S_1, S_{2a}, ..., S_{4z} and is Cohen-Macaulay).
- Classical, fundamental -and useful- Theorems
- *Theorem 1: For any linear representation of a finite group G, the algebra of invariant polynomials R^G is Cohen-Macaulay* (includes the results Schmelzer-Murrell).

- *Theorem 2: Let G a finite subgroup of $GL(V)$. Then, R^G is a polynomial algebra if and only if G is generated by pseudo-reflections (elements with precisely one eigenvalue not equal to 1).*
- Very strong restriction: most linear representations associated to nuclear permutation groups will give raise to Cohen-Macaulay non-polynomial invariant algebras !!

- *Theorem 3: Let G be the product of a reductive group over the real numbers with a finite group, let V be a linear representation of G, then the ring of invariants R^G is Cohen-Macaulay.*
- In particular, the Theorem holds whenever G is a nuclear PTRI group -that is, one may always find basic and redundant invariants to describe the invariant polynomials associated to the group and, moreover, the (purely algebraic) process of taking the permutation invariants in the Cohen-Macaulay algebra of $O(3)$-invariants preserves the Macaulay properties of the ring.

Application to $CH4$

- Let us illustrate how these results apply concretely to $CH4$.
- In each particular case, the abstract algebraic methods should be adapted to take advantage numerically, as far as possible, from the particular symmetry properties of the molecule -eg, by choosing, from the beginning a good family of symmetry-adapted coordinates.
- We write $\mathcal{P}$ for the algebra of $O(3)$-invariants and $G = \Sigma_4$ for the hydrogen nuclei permutation group.

- From the previous theorems, we deduce that the $O(3) \times G$-invariant algebra $\mathcal{P}^G$ has a so-called Hironaka decomposition:

  $$\mathcal{P}^G = \mathbf{R}[\mathbf{f_1}, ..., \mathbf{f_m}] \oplus \mathbf{R}[\mathbf{f_1}, ..., \mathbf{f_m}]\mathbf{g_1} \oplus \cdots \oplus \mathbf{R}[\mathbf{f_1}, ..., \mathbf{f_m}]\mathbf{g_p}.$$

  where the f_i are $3N - 6$ algebraically independent invariant polynomials and the g_i auxiliary invariants.

- The (bi)-set $\{f_1, ..., f_m; g_1, ..., g_p\}$ is usually refered to as an integrity basis for $\mathcal{P}^G$.

The total number $(m+p)$ of polynomials to compute in order to get an explicit Hironaka decomposition of $\mathcal{P}^G$ follows from the computation of the Molien series of the algebra:

$$Hilb(\mathcal{P}^G, t) = \sum_{i \geq 0} dim\mathcal{P}_i^G \, t^i, \tag{1}$$

The Molien series also reads:

$$Mol(t) = \frac{1 + t^{deg(g_1)} + ... + t^{deg(g_p)}}{(1 - t^{deg(f_1)})...(1 - t^{deg(f_m)})}. \tag{2}$$

So, if the degrees of the basic invariants are given, then the quantity, $Mol(t) \cdot (1 - t^{deg(f_1)})...(1 - t^{deg(f_m)})$ determines the number of auxiliary invariants of each degree.
The problem of generating $\mathcal{P}^G$ comes down to the computation of a complete set of such auxiliary invariants given a set of basic invariants.

The set of basic and auxiliary coordinates $\{S_1, S_{2a}, S_{2b}, S_{3x}, S_{3y}, S_{3z}, S_{4x}, S_{4y}, S_{4z}; S_5\}$ is well adapted to the permutation group action: S_1 and S_5 transform as the trivial representation of Σ_4, whereas the representation of Σ_4 on the vector space $\mathbf{R} < S_{2a}, ..., S_{4z} >$ generated by $S_{2a}, ..., S_{4z}$ splits into a direct sum of irreducible representations:

$$\mathbf{R} < S_{2a}, S_{2b} > \oplus \mathbf{R} < S_{3x}, S_{3y}, S_{3z} > \oplus \mathbf{R} < S_{4x}, S_{4y}, S_{4z} > .$$

The computation of the Molien series follows:

$$\frac{(1-t^2)^3(1-t^3)^3(1-t^4)^2}{1+t+t^2+t^3} \cdot Mol(t) =$$

$$1+t^2+5t^3+9t^4+12t^5+18t^6+21t^7+24t^8+26t^9+15t^{10}+8t^{11}+4t^{12}$$

Next step: constructing a family of algebraically independent generators.

- Due to the decomposition

  $$\mathbf{R} < S_{2a}, S_{2b} > \oplus \mathbf{R} < S_{3x}, S_{3y}, S_{3z} > \oplus \mathbf{R} < S_{4x}, S_{4y}, S_{4z} >,$$

  the algebraically independent polynomials f_i can be searched in the invariant subalgebras $\mathbf{R}[S_{2a}, S_{2b}]^{\Sigma_4}$, $\mathbf{R}[S_{3x}, S_{3y}, S_{3z}]^{\Sigma_4}$, and $\mathbf{R}[S_{4x}, S_{4y}, S_{4z}]^{\Sigma_4}$.

- However, the corresponding representations are generated by reflections -so that the 2nd structure theorem applies: these algebras are polynomial algebras. The corresponding basic invariants are known -they have already appeared in the litterature.

1. Degree 2:

$$f_1 = I_2^2 := \frac{S_{2a}^2 + S_{2b}^2}{\sqrt{2}}$$

$$f_2 = I_3^2 := \frac{S_{3x}^2 + S_{3y}^2 + S_{3z}^2}{\sqrt{3}}$$

$$f_3 = I_4^2 := \frac{S_{4x}^2 + S_{4y}^2 + S_{4z}^2}{\sqrt{3}}$$

2. Degree 3:

$$f_4 = I_2^3 := \frac{S_{2a}^3 - 3S_{2b}^2 S_{2a}}{\sqrt{10}}$$

$$f_5 = I_3^3 := S_{3x} S_{3y} S_{3z}$$

$$f_6 = I_4^3 := S_{4x} S_{4y} S_{4z}$$

3. Degree 4:

$$f_7 = I_3^4 := \frac{S_{3x}^4 + S_{3y}^4 + S_{3z}^4}{\sqrt{3}}$$

$$f_8 = I_4^4 := \frac{S_{4x}^4 + S_{4y}^4 + S_{4z}^4}{\sqrt{3}} .$$

Inductive determination of the auxiliary invariants

- Concretely, it can be shown easily that one can choose auxiliary invariants of the algebra of polynomial invariants that are homogeneous when considered as polynomials over any of the set of variables: $\{S_{2a}, S_{2b}\}$, $\{S_{3x}, S_{3y}, S_{3z}\}$, $\{S_{4x}, S_{4y}, S_{4z}\}$. We say that such a polynomial is multi-homogeneous and write respectively $d_2(P), d_3(P), d_4(P)$ for the partial degrees with respect to the three sets of variables.

- For example, here are two typical invariant polynomials, respectively of multidegrees $(0, 1, 2)$ and $(0, 3, 2)$:

$$S_{3z}S_{4x}S_{4y} + S_{3y}S_{4x}S_{4z} + S_{3x}S_{4y}S_{4z}$$

$$S_{3z}^3S_{4x}S_{4y} + S_{3y}^3S_{4x}S_{4z} + S_{3x}^3S_{4y}S_{4z}.$$

  We denote by $Bas(d_2, d_3, d_4)$ the set of all the monomials in the basic invariants of partial degrees d_2, d_3, d_4.

- The general structure of the algorithm for computing auxiliary invariants reads as follows. As already alluded at, the algorithm is by induction (with respect to the degrees of generators). The algorithm constructs for each multi-degree (d_2, d_3, d_4) a complete set $Aux(d_2, d_3, d_4)$ of auxiliary invariants.

- Initialization of the algorithm: compute, inductively, for all multidegrees (d_2, d_3, d_4) the corresponding set of multi-homogeneous monomials in the basic, algebraically independent, invariants: $Bas(d_2, d_3, d_4)$.
  Set $Aux(d_2, d_3, d_4) = \{1\}$ for $(d_2, d_3, d_4) = (0, 0, 0)$, and $Aux(d_2, d_3, d_4) = \emptyset$ in all other cases.
- For $1 \leq n \leq 12$, assume also that the auxiliary invariants of total degree $n - 1$ have been constructed. Put the lexicographical order on the multi-degrees (d_2, d_3, d_4), such that $d_2 + d_3 + d_4 = n$.

- For $(0, 1, n-1) \leq (d_2, d_3, d_4) \leq (n-1, 1, 0)$, construct all the invariant monomials in the basic invariants and the auxiliary invariants that can be obtained as the product of an element of $Bas(d_2', d_3', d_4')$ with an element of $Aux(d_2", d_3", d_4")$ such that $d_2 = d_2' + d_2", d_3 = d_3' + d_3", d_4 = d_4' + d_4"$. Call $Inv(d_2, d_3, d_4)$ this set of monomials.

- Using the Reynolds operator associated to the nuclear symmetric group Σ_4,

$$\frac{1}{Card(G)} \sum_{g \in \Sigma_4} g$$

which is a projector from the algebra of polynomials in the $S_{2a}, ..., S_{4z}$ to the algebra of Σ_4-polynomial invariants, construct an ordered set of generators $B(d_2, d_3, d_4) = \{b_1, ..., b_k\}$ for the vector space of Σ_4-polynomial invariants of multi-degree (d_2, d_3, d_4).

- Test recursively if the elements of $B(d_2, d_3, d_4)$ belong to the linear span of $Inv(d_2, d_3, d_4)$. If the element b_i belongs to $Inv(d_2, d_3, d_4)$, proceed to b_{i+1} as long as $i < k$. Else, set $Inv(d_2, d_3, d_4) := Inv(d_2, d_3, d_4) \cup \{b_i\}$, $Aux(d_2, d_3, d_4) := Aux(d_2, d_3, d_4) \cup \{b_i\}$ and proceed to b_{i+1} as long as $i < k$. When all the b_i have been considered, a complete family of auxiliary invariants of multi degree (d_2, d_3, d_4) has been obtained, $Aux(d_2, d_3, d_4)$.
- Proceed to the next multidegree, (d_2, d_3, d_4), in the lexicographical order till the process terminates.

Conclusions

- Due to the structure theorems for invariant algebras and CohenMacauly algebras, the results apply for any P.E.S and molecule.
- Working out the particular case of CH_4 show that one can take advantage at various levels of the structure of the molecules to speed up the algorithms -and optimize the internal structure of the integrity basis.
- Although the algorithms work in full generality, this makes the case-by-case computation of integrity basis an interesting process on its own.

- This algebraic/geometric optimization is most probably interesting for the understanding of the symmetry constraints for the geometry of the P.E.S.
- Perspectives: extension of the methodology to the dipole moment surfaces (DMS).