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Building symmetric polynomials to fit a potential energy surface: application to an A_2B_2 molecule

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Abstract We present a method to build potential energy surfaces with the correct permutational symmetry of identical atoms. It is explained and applied to an A_2B_2 molecular system. This method allows us to use different reference geometries, which are often needed in large molecules.

1 Introduction

Due to the invariance of the electronic hamiltonean, the Potential Energy Surface (PES) for a molecular system should be invariant to the permutation of identical atoms. Despite the development of the theory of invariant functions by Molien in 1897 [1] its application to physical science was not immediate. However, the construction of invariant functions of finite transformation groups has long been applied to crystal point groups [2–4], since the thermodynamic potentials of any symmetric system need to be invariant to the group of its symmetry.

To our knowledge, the introduction of symmetry into the PESs was first proposed by Murrell and co-workers when building a PES for the ozone molecule [5]. These

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ideas have also been applied to A_2B molecules [6] and generalised to other systems [7,8]. The basic idea on building a potential symmetric to the permutations of the equivalent coordinates was to define the potential in terms of the internuclear distances, or displacement coordinates from a reference geometry, and write the polynomial function in terms of symmetric combinations of these displacements, obtained by using projection operators. In those works the reference structure was chosen as a configuration with the highest symmetry of the molecule with a perimeter equal to that of the equilibrium structure.

Later, Schmelzer and Murrell [9] pointed out that the permutation group of similar atoms should be used instead of the permutation group of the coordinates, *i.e.* "the topological relations between the coordinates and the nuclei have to be preserved". In this work the authors apply the Molien's theorem to derive the analytic form of an invariant potential function and apply it to tetra-atomic homonuclear molecules, a X_4 system, correcting an earlier work about this subject [7]. When applied to an A_2B system [10], this method gives simpler polynomial than previous works on H_2O ($\tilde{X}$, $^1A'$) [11], H_2O ($\tilde{a}$, $^3A''$) [12] and HO_2 ($\tilde{X}$, $^2A''$) [6,13]. These ideas have also been applied by Ischtwan and Peyerimhoff to AX_n ($n = 3, 4$) molecules [14].

Collins and Parsons [15] generalised these ideas to the use of cartesian coordinates when describing a PES. In their work they modified the Molien's theorem to apply to the translation-rotation-inversion-permutation group and showed how to define $3N-6$ algebraically independent internal coordinates from symmetry combinations of the $3N$ cartesian coordinates. A development of these ideas and application to XY_4 molecules can be found in work for Chena and Patras [16].

Nowadays, where potential energy surfaces for systems with four or more atoms became feasible, the importance of including the correct permutation symmetry of identical atoms turns out to be a crucial task [17]. Bowman and co-workers use the Magma computer algebra system to determine the dimension of the relevant space of invariant polynomials at each degree through the construction of a Hilbert Series for the $H_5O_2^+$ system. Their invariant polynomial for this 7-atom system is built from the 21 internal coordinates and not from the 15 algebraically independent ones. In spite of using 6 redundant coordinates, they did not find out any problem on the fitting procedure.

In addition, an accurate fitting of the energies often requires the use of several functions centered in different reference geometries, *e.g.* minima and saddle points. These reference geometries may not satisfy the permutation requirements of the PES, which do not allow the use of displacement coordinates in the way suggested by Murrell and collaborators [6].

The procedure to define a set of symmetric coordinates and the integrity basis is general and can be applied to any system. In this work we illustrate this procedure by the construction of a symmetric polynomial for an A_2B_2 system. In addition we propose a way to include different reference geometries in the potential energy function. Note that this is a 4-atom system where the number of internal coordinates equals the degrees of freedom. A preliminary version of this work has been presented at the 2012 National Meeting of the Portuguese Mathematical Society [18].

2 The permutation point group

We start considering the A_2B_2 system as illustrated in Fig. 1 in which the atoms are labeled as A_1, A_2, B_1 and B_2. To describe the system we chose a set of six internal coordinates, each one corresponding to a distance between two atoms. These 6 internal coordinates are labeled as R_1, R_2, R_3, R_4, R_5 and R_6 where R_1 stands for the distance between the two A atoms, R_2 between the two B atoms and R_3, R_4, R_5 and R_6 represents the four possible distances between the A and B atoms. Using this labels we can define the Complete Nuclear Permutation (CNP) group which represents all possible permutations of identical atoms in the system. Since we have two sets of identical atoms, the CNP group will be given by the direct product of the groups $S_2^{(A)}$ and $S_2^{(B)}$ and can be represented as $S_2^{(A)} \otimes S_2^{(B)}$ [19], which is isomorphic to the D_2 point group. In this way the CNP consists of a total of four permutation operations including the identity E, the exchange of two A atoms, $(A_1\ A_2)$, the exchange of two B atoms, $(B_1\ B_2)$ and the simultaneous exchange of atoms A and B $(A_1\ A_2)(B_1\ B_2)$. Each of these symmetry operations acts on the molecule changing, or not, the order of the internal coordinates. Exemplifying, the permutation operation of two A atoms is described by:

$$(A_1\ A_2) = \begin{pmatrix} R_1 & R_2 & R_3 & R_4 & R_5 & R_6 \\ R_1 & R_2 & R_5 & R_6 & R_3 & R_4 \end{pmatrix}. \tag{1}$$

It turns out that, by applying this operation the internal coordinates R_1 and R_2 remain the same but all the others change its position, R_3 assumes the value of R_5 and R_4 assumes the value of R_6.

The four permutation operations for this system can be described in a matricial 6-dimensional representation, which constitutes the $\Re$ representation of this permutation group for this basis of coordinates.

Fig. 1 Bonds used in the present work for an A_2B_2 system
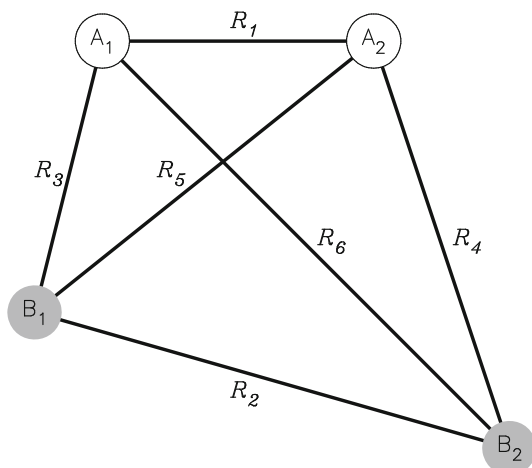
$$E = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad (A_1 A_2)(B_1 B_2) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

$$(A_1 A_2) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \quad (B_1 B_2) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} .$$

$$(2)$$

Using the projection operator we can see that this representation spans three times the A irreductible representation and once each of the B_1, B_2 and B_3 irreductible representations of this group.

3 Invariant polynomial

Three question must be answered in order to build a polynomial invariant to the group operations, using a given set of coordinates: what is the smallest number of terms, called integrity basis, that can be used to build such polynomial; how many terms of each degree shall we use; how can we define this integrity basis.

Molien [1] has shown that by using a set of independent coordinates, ξ_i, any invariant polynomial of a finite group can be generated by the expression

$$\phi_G(\lambda) = \frac{1}{|G|} \sum_{g \in G} \frac{1}{det[\mathbf{I} - \lambda \mathbf{M}(g)]}, \tag{3}$$

where $\mathbf{I}$ is the identity matrix, λ is a dummy variable, g is an operation of the group G, $|G|$ is the order of the group and $\mathbf{M}(g)$ corresponds to the matrices of the representation in the ξ_i basis, shown above. Applying this expression to our $\mathfrak{R}$ representation, Eq. 2, we have

$$\phi_G(\lambda) = \frac{1}{4} \left[\frac{1}{(1-\lambda)^6} + \frac{3}{(1-\lambda)^2 (1-\lambda^2)^2} \right], \tag{4}$$

which, as showed by Molien, can be rearranged to

$$\phi_G(\lambda) = \frac{1 + \lambda^3}{(1-\lambda)^3 (1-\lambda^2)^3}, \tag{5}$$

with positive coefficients in the numerator.

This last equation, Eq. 5, can be expanded in terms of the dummy variable λ, leading to

$$\phi_G(\lambda) = 1 + 3\lambda + 9\lambda^2 + 20\lambda^3 + 42\lambda^4 + 78\lambda^5 + \cdots. \tag{6}$$

Equation 6 gives us the information relative to the number of terms of each degree that we will need in order to build an invariant polynomial. So, for this tetratomic system with two pairs of identical atoms, we will have an invariant of degree 0; 3 invariants of degree 1; 9 of degree 2 and so on.

4 The integrity basis

Any invariant polynomial function of a finite group can be developed in terms of a finite number of invariant polynomials, called integrity basis. We now refer the way we can obtain information about this integrity base from Eq. 5.

We can rewrite Eq. 5 displaying it as product of seven factors,

$$\phi_G(\lambda) = (1 + \lambda^3) \times \frac{1}{(1 - \lambda)} \times \frac{1}{(1 - \lambda)} \times \frac{1}{(1 - \lambda)} \times \frac{1}{(1 - \lambda^2)}$$
$$\times \frac{1}{(1 - \lambda^2)} \times \frac{1}{(1 - \lambda^2)}. \tag{7}$$

Since the power series expansion of $\frac{1}{1-x}$ gives rise to the geometric series of x, *i.e.* a sum of powers of x,

$$\frac{1}{(1 - x)} = \sum_{i=0}^{\infty} x^i = 1 + x + x^2 + x^3 + x^4 + \cdots, \tag{8}$$

we can, in the same way, expand each of the fractions of Eq. 7. The expansion leads to a product of seven polynomials which, after multiplication, yields the Eq. 6. Note that these seven polynomials correspond to: one polynomial defined as $1 + \lambda^3$; three others given by the complete expansions of a first degree term, $1 + \lambda + \lambda^2 + \cdots$, and the other three result from the expansion of the second degree terms, $1 + \lambda^2 + \lambda^4 + \cdots$. With this information in mind, we are able to define the size of the integrity basis and the number of its invariants.

Replacing the dummy variable λ, Eq. 7 can be rewritten as

$$\phi_G = (1 + a^3) \times (1 + b + b^2 + \cdots) \times (1 + c + c^2 + \cdots) \times (1 + d + d^2 + \cdots)$$
$$\times (1 + e^2 + e^4 + \cdots) \times (1 + f^2 + f^4 + \cdots) \times (1 + g^2 + g^4 + \cdots)$$
$$= 1 + (b + c + d) + (b^2 + c^2 + d^2 + bc + bd + cd + e^2 + f^2 + g^2) + (a^3$$
$$+ b^3 + b^2c + b^2d + bcd + be^2 + \cdots. \tag{9}$$

This equation shows that the invariant polynomial of Eq. 6 can be built from six algebraically independent primary invariants, three of the first degree, b, c and d,

Table 1 Algebraically independent and auxiliary invariants for an A_2B_2 system

Degree			
1	$\varphi_1(\mathbf{r}) = \rho_1 = R_1$	$\varphi_2(\mathbf{r}) = \rho_2 = R_2$	$\varphi_3(\mathbf{r}) = \rho_3$
2	$\varphi_4(\mathbf{r}) = \rho_4^2$	$\varphi_5(\mathbf{r}) = \rho_5^2$	$\varphi_6(\mathbf{r}) = \rho_6^2$
3	$\varphi_7(\mathbf{r}) = \rho_4\rho_5\rho_6$		

Table 2 Invariant polynomial terms constructed from the integrity basis, Eq. 1

Degree	Number	Terms
0	1	Constant
1	3	$\varphi_1(\mathbf{r});\ \varphi_2(\mathbf{r});\ \varphi_3(\mathbf{r})$
2	9	$\varphi_1(\mathbf{r})^2;\ \varphi_1(\mathbf{r})\varphi_2(\mathbf{r});\ \varphi_1(\mathbf{r})\varphi_3(\mathbf{r});$ $\varphi_2(\mathbf{r})^2;\ \varphi_2(\mathbf{r})\varphi_3(\mathbf{r});\ \varphi_3(\mathbf{r})^2;$ $\varphi_4(\mathbf{r});\ \varphi_5(\mathbf{r});\ \varphi_6(\mathbf{r})$
3	20	$\varphi_1(\mathbf{r})^3;\ \varphi_1(\mathbf{r})^2\varphi_2(\mathbf{r});\ \varphi_1(\mathbf{r})^2\varphi_3(\mathbf{r});$ $\varphi_1(\mathbf{r})\varphi_2(\mathbf{r})^2;\ \varphi_1(\mathbf{r})\varphi_2(\mathbf{r})\varphi_3(\mathbf{r});\varphi_1(\mathbf{r})\varphi_3(\mathbf{r})^2;$ $\varphi_1(\mathbf{r})\varphi_4(\mathbf{r});\ \varphi_1(\mathbf{r})\varphi_5(\mathbf{r});\ \varphi_1(\mathbf{r})\varphi_6(\mathbf{r});$ $\varphi_2(\mathbf{r})^3;\ \varphi_2(\mathbf{r})^2\varphi_3(\mathbf{r});\ \varphi_2(\mathbf{r})\varphi_3(\mathbf{r})^2;\varphi_2(\mathbf{r})\varphi_4(\mathbf{r});$ $\varphi_2(\mathbf{r})\varphi_5(\mathbf{r});\ \varphi_2(\mathbf{r})\varphi_6(\mathbf{r});\ \varphi_3(\mathbf{r})^3;\ \varphi_3(\mathbf{r})\varphi_4(\mathbf{r});$ $\varphi_3(\mathbf{r})\varphi_5(\mathbf{r});\ \varphi_3(\mathbf{r})\varphi_6(\mathbf{r});\ \varphi_7(\mathbf{r})$
4	42	...

three of the second degree , e^2, f^2 and g^2, and an auxiliary secondary invariant of the third degree, a^3, which can only be used once in each monomial. Notice that the number of primary invariants equals the number of independent coordinates used to generate the representation.

So far we have already answered two of the above questions, the dimension of the integrity basis and the number of terms of each degree that we can used to construct the invariant polynomial. Now we refer to the definition of the integrity basis. There are different ways to define it [20] and here we use the character table of the D_2 group in a way similar to the one used by Schmelzer and Murrell [9]. Using the projection operator,

$$\mathcal{P}^i = \frac{n_i}{|G|} \sum_g \chi_g^{(i)} \Theta_g \tag{10}$$

where $\chi_g^{(i)}$ represents the trace of the operation g in the irreducible representation i, and the group operations, Θ_g described by Eq. 2, we can construct combinations of the R_1, R_2, R_3, R_4, R_5 and R_6 coordinates that behave as the different irreducible representations of the D_2 point group:

$$\rho_1 = R_1 \quad \in A$$
$$\rho_2 = R_2 \quad \in A$$

$$\rho_3 = \frac{1}{2}(R_3 + R_4 + R_5 + R_6) \quad \in A \tag{11}$$

$$\rho_4 = \frac{1}{2}(R_3 + R_4 - R_5 - R_6) \quad \in B_1$$

$$\rho_5 = \frac{1}{2}(R_3 - R_4 + R_5 - R_6) \quad \in B_2$$

$$\rho_6 = \frac{1}{2}(R_3 - R_4 - R_5 + R_6) \quad \in B_3$$

The two diatomic distances R_1 and R_2 belong to the totally symmetric representation A since they do not exchange when any of the four permutation operations is applied to the system. The sum of R_3, R_4, R_5 and R_6, denoted as ρ_3, also belong to the totally symmetric representation A but the other three combinations do not. To build totally symmetric coordinates terms from the ρ_4, ρ_5 and ρ_6 we can use the direct product multiplication table of the D_2 group. It can be easily shown that ρ_4^2, ρ_5^2 and ρ_6^2 constitute the three invariant terms of the second degree and that $\rho_4\rho_5\rho_6$ is the third degree invariant term. In short, the polynomial will be constructed as combinations of the seven integrity basis terms described in Table 1. In Table 2 we display the first polynomial terms to use.

5 Reference geometry

It is common practice to use a polynomial term multiplied by a decay factor as a functional form for a PES. The decay term warrants that the PES vanishes when all the atoms are far appart or, in a many-body expansion, when one atom of the n-body term is far from any other. Both the polynomial and the decay terms must be invariant to any symmetry operation of the system. Both terms are often computed using displacement coordinates from some reference geometry usually chosen as the equilibrium position of the atoms or a saddle point configuration. Frequently, the reference geometries do not have the necessary symmetry restrictions and cannot be used to define the displacement coordinates. To deal with this problem, Murrell and collaborators [6] proposed to use a symmetryzed reference built from the original data. For example, for the HO_2 radical they proposed to use, as reference structure, a C_{2v} configuration with the same O–O distance and perimeter as the equilibrium structure. Within this approach at least one of the coordinates does not vanish at the reference. Alternatively, instead of using displacement coordinates we propose to use displacement integrity basis, *i.e.*, each term of the integrity basis should be subtracted by the equivalent term computed at the reference geometry and the polynomial and decay terms should be built by using these displacement integrity basis. The subtraction of a constant value does not modify the invariance of the polynomial. As an example, we give in Table 3 the displacement integrity basis for an A_2B_2 system with a reference geometry defined by six $R_{i,ref}$ distances. Within this approach, all the integrity basis terms will vanish at the reference geometry, remaining only the constant term. As there are no restrictions to the reference geometry, this can be easily implemented to do a multifunctional fit using a different reference geometry for each function.

Table 3 Displacement integrity basis

Degree			
1	$\varphi_1(\mathbf{r}) = \rho_1 - \rho_{1,\,ref}$	$\varphi_2(\mathbf{r}) = \rho_2 - \rho_{2,\,ref}$	$\varphi_3(\mathbf{r}) = \rho_3 - \rho_{3,\,ref}$
2	$\varphi_4(\mathbf{r}) = \rho_4^2 - \rho_{4,\,ref}^2$	$\varphi_5(\mathbf{r}) = \rho_5^2 - \rho_{5,\,ref}^2$	$\varphi_6(\mathbf{r}) = \rho_6^2 - \rho_{6,\,ref}^2$
3	$\varphi_7(\mathbf{r}) = \rho_4\rho_5\rho_6 - \rho_{4,\,ref}\rho_{5,\,ref}\rho_{6,\,ref}$		

6 Conclusion

Although the theory of invariant functions is well described in the literature, its application to chemical problems is not a straightforward task. We have shown how to construct a PES invariant to the permutational symmetry of identical atoms and applied it to the A_2B_2 system. We have also shown a recipe to include non-symmetrical reference geometries in those PESs. These ideas have been successfully applied in the fitting of four-body terms for the H_2O_2 ($\tilde{X}$, ^1A) molecule.

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