Reduced coordinates on the configuration space of three and four atoms

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A framework for constructing three- and four-body interatomic potentials is proposed. The study is motivated by a need for an understanding of the morphology of these potentials and consequently the morphology of the Born-Oppenheimer energy surface (i.e., the location of the surface minimum and saddle points). Invariant coordinate systems on the configuration space of three and four atoms are therefore developed which allow the morphology of three- and four-body terms to be chosen. Direct applications of these coordinates include the construction of interatomic potentials and an analysis of the local geometry around an atom in a crystal.

I. INTRODUCTION

Classical potentials have been used extensively to study the properties of various crystals, including those with covalent bonding. Some of these potentials, such as Tersoff's for silicon,[1] were derived from the tight-binding approach to total-energy calculations. This method has the advantage of providing a mathematical form that can be fitted to experimental data. Other approaches have been more phenomenological, such as the one proposed by Keating.[2] In this approach the total energy is expanded as a sum of many-body terms. Construction of the terms in this expansion, which together reproduce the properties of crystalline silicon, is then dependent on an intuitive understanding of the space containing many atoms.

The goal of this paper is to present coordinate systems for the configuration space of three and four atoms that will provide the geometrical insight required to construct many-body terms. The improvement is twofold. First, the use of these coordinates allows the morphology of the potential to be chosen. Second, the use of a radius in the three- or four-body configuration space permits definition of specific cutoff radii for the three- and four-body terms. This latter condition results in a significant reduction in the number of three- or four-body terms that need to be accessed, thus increasing the efficiency of the computation.[3]

This paper is structured as follows. Sections II and III describe the motivation for deriving reduced coordinates together with a summary of the main results obtained. In Sec. IV a mathematical analysis of the problem is presented, the details of which are given in the Appendix. Section V describes the general approach for constructing the three- and four-body coordinates which are subsequently derived in detail in Secs. VI and VII. An application of the three-body coordinates to the construction of potentials in silicon is given in a companion paper.[4]

II. OBJECTIVES

The idea in constructing three- and four-body coordinates is to develop a tool that describes the three- and four-body configuration spaces in terms of their symmetry configurations, since this will, in turn, provide a better understanding of the morphology of the three- and four-body terms of the interatomic potential. The symmetries present in these spaces necessitates the existence of critical points for interatomic potentials in symmetric configurations. If a simple shape for the interatomic potential is assumed, then it could have all its saddle points on such configurations. A description of the potential's topology therefore requires a good understanding of the neighborhood of symmetry configurations. As seen below, such a description can be obtained fully in the three-body configuration space, but only partially so in the four-body case.

A p-body potential is a function defined on the configuration space of p particles, which is the space $\mathbb{R}^3\times\mathbb{R}^3\times\cdots\times\mathbb{R}^3$. Its elements are p-uplets $(u_1,u_2,\ldots,u_p)$, where u_i is a vector in $\mathbb{R}^3$ and represents the position of particle i. Notice that this space can also be viewed as $\mathbb{R}^p\otimes\mathbb{R}^3$. The symmetries relevant to a p-body term are the following.

(a) Global translations: group $\mathbb{R}^3$. This term does not depend upon the position of the p-uplet center of mass.

(b) Global rotations and inversion: group O(3). This term does not depend upon its orientation in space.

(c) Permutations of identical atoms: group S_p when the p atoms are identical, which is the case under present consideration.

The method for constructing such a potential is to use some internal coordinates which are sufficient to represent the relative atomic positions. A pair potential, for example, is seen as a function of the interatomic distance. In this case, it is easy to check that this parameter (the interatomic distance) is enough to specify the relative positions of two atoms independently of symmetries of

types (a), (b), and (c). The case of three atoms is more complex. Previous studies have used internal coordinates that describe the triangle geometry independently of symmetries of types (a) and (b). Symmetry of type (c) is then taken care of by symmetrizing the potential itself. The Stillinger-Weber potential for silicon,[5] for example, is constructed using two interatomic distances and one angle. More precisely, the triangle (i,j,k) is represented by the distances $d(i,j)$, $d(j,k)$ and the angle $\sphericalangle ijk$. Hence, it is seen that substituting i for k does not change these coordinates, but that substituting i for j does. In fact, this coordinate system places special emphasis on the atom j. A symmetric three-body potential is then obtained as

$$V_3=\tfrac{1}{3}(V_{ijk}+V_{kij}+V_{jki}) . \tag{1}$$

The problem with this method now appears: Insight into the shape of V_{ijk} (the location of the minimum in particular) is lost in V_3. Compared to V_{ijk}, the location of the V_3 minimum cannot be expressed in terms of any of the three possible coordinates systems, which emphasize only one of the i, j, or k.

In order to avoid this problem in the present study, coordinate systems have been constructed that are invariant under the symmetries (a), (b), and (c) with specific applications to three and four atoms. These coordinates are called reduced coordinates for they are coordinates of the reduced configuration space, which is the configuration space divided by symmetries (a), (b), and (c). Any function of these reduced coordinates can then be considered as a p-body term (where p is equal to 3 or 4). Construction of these coordinates will provide improved insight into the topology of the potential and subsequently enable greater use of geometrical intuition in the modeling of condensed matter.

III. STATEMENT OF MAIN RESULTS

A. Three-body configuration space

Reduced coordinates are constructed in the *three-body configuration space,* which map this space on the set $[0,+\infty)\times[0,1]\times[0,1]$. They are denoted as

$$(r,s_1,s_2) .$$

The first coordinate is a radius in the reduced three-body configuration space. It defines the spatial extension of the configuration. The two other coordinates define the geometry of the configuration. They can be expressed in terms of atomic coordinates as

$$(r,s_1,s_2)=(r,\sin^2(3\theta/2),\sin(2\varphi)) , \tag{2}$$

with

$$r^2=A_1^2(X)+A_2^2(X)+A_3^2(X) , \tag{3}$$

$$\sin\theta=\frac{A_3(X)}{[A_2^2(X)+A_3^2(X)]^{1/2}} , \qquad \sin\theta=\frac{A_3(X)}{[A_2^2(X)^2+A_3^2(X)^2]^{1/2}} , \tag{4}$$

$$\sin\varphi=\frac{[A_2^2(X)+A_3^2(X)]^{1/2}}{r}, \quad \cos\varphi=\frac{A_1(X)}{r} , \tag{5}$$

where

$$A_1(X)=X_1^2+X_2^2 , \quad A_2(X)=X_1^2-X_2^2 , \quad A_3(X)=2\mathbf{X}_1\cdot\mathbf{X}_2 , \tag{6}$$

with

$$\begin{bmatrix}X_0\\X_1\\X_2\end{bmatrix}=\begin{bmatrix}(1/\sqrt{3})(u_1+u_2+u_3)\\(1/\sqrt{2})(u_1-u_2)\\(1/\sqrt{6})(u_1+u_2-2u_3)\end{bmatrix} , \tag{7}$$

where (u_1,u_2,u_3) are the atomic positions in $\mathbb{R}^3$.

The symmetry configurations then have these equations:

Equilateral triangles	$s_2=0$ (one dimensional)
Isosceles triangles	
Obtuse	$s_1=0$ (two dimensional)
Acute	$s_1=1$ (two dimensional)
Linear configurations	$s_2=1$ (two dimensional)

Note that the coordinate s_1 is not defined when $s_2=0$ (equilateral triangles). Also, the half-planes $s_1=0$ and $s_1=1$ are the two halves of the same plane (isosceles configurations) which intersect on the line of equilateral triangles. These two conditions impose restrictions on the functional form of the three-body term.

The description that is therefore obtained is one of a regular dihedral with well-defined faces, edges, and corners, thus making an analysis of the three-body term topology possible.

B. Four-body configuration space

Reduced coordinates are constructed in the *four-body configuration space.* When expressed in terms of Demazure's polynomials (see the Appendix and Sec. IV below), they are

$$\begin{aligned} &x_1=\sqrt{r_2}, \quad x_4=[r_7^2-(r_4/3)^3]/r_2^3, \quad x_7=r_7/(r_2)^{3/2} ,\\ &x_2=(r_1/\sqrt{r_2})-\sqrt{3}, \quad x_5=r_4(r_5-2r_7-r_3)/(r_2)^{5/2}, \quad x_8=r_8/r_2^2 ,\\ &x_3=(r_3/(r_2)^{3/2})-1/3\sqrt{3}, \quad x_6=r_6/r_2^2 . \end{aligned} \tag{8}$$

Demazure's polynomials are

$$\begin{aligned} &r_1=A_2+B_2+C_2, \quad r_5=A_2A_1^2+B_2B_1^2+C_2C_1^2 , \\ &r_2=A_2^2+B_2^2+C_2^2, \quad r_6=A_2^2A_1^2+B_2^2B_1^2+C_2^2C_1^2 , \\ &r_3=A_2B_2C_2, \quad r_7=A_1B_1C_1 , \\ &r_4=A_1^2+B_1^2+C_1^2, \quad r_8=A_1^4+B_1^4+C_1^4 , \end{aligned} \tag{9}$$

where

$$\begin{aligned} &A_1=\mathbf{X}_2\cdot\mathbf{X}_3, \quad A_2=X_1^2 , \\ &B_1=\mathbf{X}_1\cdot\mathbf{X}_3, \quad B_2=X_2^2 , \\ &C_1=\mathbf{X}_1\cdot\mathbf{X}_2, \quad C_2=X_3^2 , \end{aligned} \tag{10}$$

and

$$\begin{bmatrix} X_0 \\ X_1 \\ X_2 \\ X_3 \end{bmatrix} = \begin{bmatrix} \frac{1}{2}(u_1+u_2+u_3+u_4) \\ \frac{1}{2}(u_1-u_2+u_3-u_4) \\ \frac{1}{2}(u_1-u_2-u_3+u_4) \\ \frac{1}{2}(u_1+u_2-u_3-u_4) \end{bmatrix} , \tag{11}$$

where (u_1,u_2,u_3,u_4) are the atomic positions of the four atoms in $\mathbb{R}^3$.

The reduced coordinates map this space onto a hypersurface of $\mathbb{R}^+\times K$, where K is the product of six bounded intervals. The boundaries of this surface are not all understood so that a complete analysis of the topology of a four-body term is still not possible. However, this choice of coordinates allows an understanding of the vicinity of some symmetry configurations of interest for the description of a simple crystalline solid such as silicon. Their equations are

Tetrahedron	$x_2=x_3=x_4=x_6=x_7=0$
Triangular pyramid	$x_2=x_3=x_4=0$
Triangular star	$x_2=x_3=x_4=x_5=0$

The derived coordinates therefore permit construction of four-body terms that reach their lowest values for these configurations.

IV. MATHEMATICAL BACKGROUND

Remark. In the following the term "coordinate system" will be used in an extended sense. A coordinate system (p-body coordinates) will be a set of invariants [through symmetries (a), (b), and (c)] that are sufficient to define the relative positions of atoms. The coordinate system will be said to be proper if it comprises as many invariants as there are degrees of freedom in the system, that is, $3p-6$ for p atoms. In this case, the invariants are independent: There does not exist any relationship between them.

The problem of dividing the configuration space by the orthogonal group O(3) has been addressed by Von Neumann,[6] who proved that any function defined on the configuration space which is symmetric under O(3) is in fact a function of the scalar products $q_{ij}=(u_i|u_j)$. Indeed, he showed that any polynomial in the atomic coordinates that is symmetric under the action of O(3) can be written as a polynomial in the q_{ij}'s. The q_{ij}'s therefore define $p(p+1)/2$ invariants, which are independent when p equals 3.

The condition that these polynomials are also symmetric under the action of translations is then equivalent to p conditions on the q_{ij}'s, which are that the sum of each row of the matrix (q_{ij}) is equal to zero (it is equivalent to stating that the u_i's are taken in a barycentric reference state). This implies that, within each row, the diagonal term is equal to minus the sum of the off-diagonal terms. Hence, the configuration space divided by the rotations and the translations is fully described by the off-diagonal terms [in number $p(p-1)/2$], which are independent when p equals 3 or 4 (they form a proper coordinate system for the configuration space divided by rotations and translations).

The problem of dividing further by the finite group of permutations is more difficult. The method used to achieve this goal is the following. The algebra of polynomials in the q_{ij}'s, $i>j$, is considered and the structure of the subalgebra of polynomials symmetric under the atomic permutations (which induce a subgroup of the full permutation group of the q_{ij}'s) is studied. A typical result that is required is something similar to what exists for the polynomials of n variables symmetric under the full permutation group. It can be shown that any symmetric polynomial can be written as a polynomial in n elementary symmetric polynomials. These elementary symmetric polynomials would then appear as a proper reduced coordinate system. Unfortunately, this result is generally wrong if a division by a subgroup of the full permutation group is made. Noether conjectured that the field of rational fractions symmetric under the specific subgroup of cyclic permutations could be generated by elementary polynomials and it is only recently that a counterexample has been found.[7]

It will be seen below that there exist three symmetric polynomials that generate the field of symmetric rational fractions in the case of three atoms and that there does not exist a set of six symmetric polynomials that would do the same thing in the case of four atoms (see the Appendix for a proof of the latter result). As far as the present problem is concerned, this means that it is possible to find proper reduced coordinates for the configuration space of three atoms and that it is not possible (at least using this approach) in the case of four. This study will, however, indicate how four-body potentials can be understood and constructed.

The final goal is to understand how the topology of the p-body potential can be chosen. This will be relatively easy if proper p-body coordinates exist. The existence of a proper p-body coordinate system is therefore the first question that needs to be addressed.

In this section some recently proved results[8] will be stated that allow this question to be answered. The description will be focused on aspects of the analysis that are directly related to the present problem. The aim is to give a global view of the structure within which the p-body coordinates are constructed and therefore to give some insight on how they can be used.

First consider $q_{ij}=(u_i|u_j)$, where u_i represents the position of atom i. Hence, i and j belong to $[1,p]$. Consider next $A_p=K[q_{ij}]$ the algebra of polynomials in the q_{ij}'s on a field K. It is seen that S_p, the permutation group of $[1,p]$ acts on A_p, through

$$\forall\sigma\in S_p,\quad \sigma(q_{ij})=(u_{\sigma(i)}|u_{\sigma(j)})\ . \tag{12}$$

Let $A_p^{S_p}$ be the ring of invariant elements of A_p through S_p. Consider then S, defined on A_p by its action on $Q\in A_p$ by

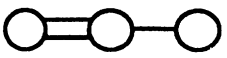
$$S(Q)=\frac{1}{\mathrm{Card}(S_p)}\sum_{\sigma\in S_p}\sigma(Q)\ . \tag{13}$$

S is a projector from A_p to $A_p^{S_p}$ (it projects any polynomial in a symmetric polynomial).

Consider next the monomials. Their image through S generates $A_p^{S_p}$. A monomial can be represented by a labeled graph such as

which represents the polynomial $q_{12}^2q_{23}$.

The image of this monomial through S can then be represented by an unlabeled graph such as



Notice that the degree of a graph is equal to the number of links and that the number of nodes has to be less than p. Among the graphs, the reduced graphs can be defined, which are the graphs with no multiple link. They are, in some sense, the simplest symmetric polynomials that can be considered.

The first question to be asked is, do the reduced graphs generate the whole algebra $A_p^{S_p}$ (so as to reduce the size of the problem)? The answer is that it is true for p less than or equal to 4 and false for p equal to 5. For this reason, the analysis is restricted to three- and four-body coordinate systems. Consider the reduced graphs with less than four nodes. They are shown in Fig. 1.

It is seen that three of the graphs in Fig. 1 have less than three nodes. As only three coordinates are needed to describe the configuration space of three atoms and, since in the case of three atoms the reduced graphs generate the whole symmetric algebra, it is concluded that the three symmetric polynomials constitute a proper coordinate system for the configuration space of three atoms. Hence, the problem of the existence of three-body coordinates is solved, and any function of these coordinates will constitute a symmetric three-body term.

The problem is now to look for the smallest set of generators in the four-body case. The fact is that the reduced space is six dimensional and that there are ten different invariants. There are therefore algebraic relations between these invariants. The problem of finding a proper coordinate system will be solved if it is possible to use these relations in order to express four of the invariants in terms of the other six.

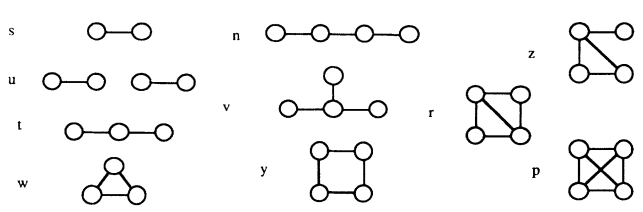


FIG. 1. Reduced graphs with less than four nodes.

This may not be possible, but suppose it is. Then, four of the invariants can be expressed as rational fractions in terms of the others. However, these rational fractions are defined only where their denominators are nonzero. In other words, the four invariants cannot be expressed in terms of the others where the denominators are equal to zero. Thus, it is, in general, not possible to use the six coordinates to distinguish points that lie on the hypersurfaces defined by the nullity of the denominators. It is, at best, expected that the coordinates allow points to be distinguished on the complementary to these hypersurfaces (which is, however, open and dense in the configuration space).

It has been shown[8] that in the present case even this is not possible. The problem is a practical one since in trying to solve for four invariants, an equation quadratic in terms of the variable that need to be extracted always appears. This implies that given six invariants, there are two ways of choosing the seventh. The six invariants are therefore not sufficient to describe fully the configuration space since they define at least two different configurations.

These two difficulties will be illustrated for the four-body coordinates that are derived below, and it will be shown how this affects the choice of the four-body potential. The reader is referred to the Appendix for a proof of the nonexistence of six generators in the four-body configuration space. To conclude this section, the main results are summarized as follows.

(i) It is possible to find a proper coordinate system in the case of three atoms that describes the totality of the configuration space (as opposed to a dense subset).

(ii) It is not possible to do so in the case of four atoms, for two reasons: (a) At least seven coordinates are needed to describe a point without ambiguity, and (b) given a choice of coordinates, there may exist hypersurfaces in the configuration space on which the coordinates will not distinguish points.

V. A CHOICE OF COORDINATE SYSTEM

The construction that is now presented was initiated independently from the one described in Sec. IV. However, it was found to be an application of the more general scheme introduced above and therefore of interest. First, it provides a convenient framework within which some of the previous results can be simply demonstrated. Second, it enables invariants to be constructed whose simple algebraic form is a decisive advantage in a computational context.

The configuration space of three atoms can be seen as $\mathbb{R}^p\otimes\mathbb{R}^3$. Elements of this space can be written as

$$\sum_{i=1}^{p}\sum_{j=1}^{3} m_{ij} e_i \otimes e_j \ ,$$

where m_{ij} represents the jth component of atom i. The interest in this formalism lies in the way the various relevant groups are then seen to act.

(a) A global translation of vector v in $\mathbb{R}^3$ is seen as a translation of vector $u \otimes v$, where u is equal to $(1, \ldots, 1)$ in $\mathbb{R}^p$.

(b) An element S in O(3) acts as $I_p \otimes S$, where I_p is the identity in $\mathbb{R}^p$.

(c) A permutation τ in S_p acts as $T \otimes I_3$, where I_3 is the identity in $\mathbb{R}^p$ and T is the matrix representation of τ on $\mathbb{R}^p$.

Division by translations and rotations

Translations are considered first. The division by global translations in $\mathbb{R}^p \otimes \mathbb{R}^3$ is performed through restriction to a subspace of $\mathbb{R}^p$. The quotient space is then $F \otimes \mathbb{R}^3$, where F is the orthogonal in $\mathbb{R}^p$ to the vectorial space generated by the p-uplet,

$$u = (1, 1, \ldots, 1) \ .$$

This is in fact equivalent to choosing a barycentric reference state. As the two other groups let $F \otimes \mathbb{R}^3$ invariant, this space can be further used for division by rotations and permutations.

It can be seen that this is equivalent to considering the off-diagonal q_{ij}'s (as in the previous approach) and the action of the quadratic forms defined on $F \otimes \mathbb{R}^3$ by the matrices $M \otimes I_3$, where M is symmetric. A sketch of the proof is the following: It is shown that the q_{ij}'s can be considered as a free family of quadratic forms. The subspace that they generate has dimension $p(p-1)/2$, which is the dimension of the space of these quadratic forms. The q_{ij}'s therefore constitute a basis of this space which is equivalent to the above statement. As the atomic permutations are seen to act on the space of quadratic forms, this space can be used further to divide by permutations.

Division by permutations

The idea of dividing by permutations is to look for a basis of the space of quadratic forms in which atomic permutations can be expressed simply. As the problem has been reduced to that of a group (the finite group of atomic permutations) acting on a vectorial space (the space of quadratic forms), it seems natural to use group theory to look for a decomposition of the space on which the group elements will be simultaneously block diagonalized. An even more powerful approach is to look for a generating family of the space that will be globally invariant under group action, using the same idea that underlies the construction of root systems for finite reflection groups.[9] It is emphasized that the purpose here is to find the simplest invariants possible in order to generate simple coordinate systems.

In the specific case of three and four atoms, such generating families of the space of quadratic forms which are globally stable under the group elements can be recognized. This provides a decomposition of the space which is the result that is required.

Step 1: Action of an atomic permutation on a quadratic form

Let $M \otimes I_3$ be the matrix of a quadratic form (hence, M is symmetric real) and $A(X)$ be the quadratic form itself. Then, for all X in $F \otimes \mathbb{R}^3$,

$$A(X) = \tfrac{1}{2}\, {}^tX \cdot M \otimes I_3 \cdot X \ . \tag{14}$$

Let τ be a permutation of S_p. It acts on $F \otimes \mathbb{R}^3$ as a linear operator $T \otimes I_3$, where T is the representation of τ on F. This, together with the previous formula, shows that A, or equivalently M, transforms with a permutation τ as

$$A(T \otimes I_3 \cdot X) = \tfrac{1}{2}\, {}^tX \cdot ({}^tT \cdot M \cdot T) \otimes I_3 \cdot X \ ,$$

$$\text{i.e., } M \rightarrow {}^tT \cdot M \cdot T \ . \tag{15}$$

Notice that since permutations are normal operators, ${}^tT$ is the matrix of the permutation τ^{-1}.

Step 2: Similarity with conjugation relation and interpretation of involutive permutations as quadratic forms

Consider the conjugation relation $\mathcal{R}$ defined between permutations by

$$\begin{aligned} &\forall \tau_1, \tau_2 \in S_p \ , \\ &(\tau_1 \mathcal{R} \tau_2) \Longleftrightarrow (\exists \tau \in S_p, \text{ such as } \tau_1 = \tau^{-1} \cdot \tau_2 \cdot \tau) \ . \end{aligned} \tag{16}$$

The classes of this relation are composed of the permutations with equal lengths of cycle. Notice now that the matrix of τ is symmetric (and therefore defines a quadratic form) if and only if it is involutive. Moreover, this property is compatible with the conjugation relation $\mathcal{R}$:

$$\begin{aligned} &\forall \tau_1, \tau_2 \in S_p \ , \\ &(\tau_1 \mathcal{R} \tau_2) \Longrightarrow (\tau_1 \cdot \tau_1 = \mathrm{Id} \Longleftrightarrow \tau_2 \cdot \tau_2 = \mathrm{Id}) \ . \end{aligned} \tag{17}$$

Hence, if one element in a class is involutive (equivalently, if its matrix is symmetric), then all the elements in the class are involutive. The desired decomposition of the space of quadratic forms will therefore be achieved if classes of permutations are found, the matrices of which generate that space. The atomic permutations will then be seen as exchanging the elements of this generating family.

Step 3: Listing the classes for three and four atoms

For the case of three atoms, it is found that the classes $\{\mathrm{Id}\}, \{\tau_{12}, \tau_{13}, \tau_{23}\}$ are needed in order to generate the whole space of quadratic forms. These two classes are found to generate a decomposition of the space of quadratic forms into two supplementary subspaces (respectively, one and two dimensional), which correspond to irreducible representations of the permutation group. The way these quadratic forms are used to construct invari-

ants is explained in Sec. VI.

For the case of four atoms, it is found that the class $\{\tau_{12},\tau_{13},\tau_{23},\tau_{14},\tau_{24},\tau_{34}\}$ is enough to generate the whole space of quadratic forms. This representation breaks down into three irreducible representations which are, respectively, one, two, and three dimensional. The corresponding coordinates are described in Sec. VII.

VI. THREE-BODY COORDINATES

When $p=3$, the following change of basis can be made to separate the global translations:

$$\begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} \rightarrow \begin{bmatrix} X_0 \\ X_1 \\ X_2 \end{bmatrix} = \begin{bmatrix} (1/\sqrt{3})(u_1+u_2+u_3) \\ (1/\sqrt{2})(u_1-u_2) \\ (1/\sqrt{6})(u_1+u_2-2u_3) \end{bmatrix} . \tag{18}$$

The space $F\otimes\mathbb{R}^3$ is then spanned by the tensors $X=(X_1,X_2)$ and F itself is spanned by the vectors

$$e_1=(1/\sqrt{2})(1,-1,0) \quad \text{and} \quad e_2=(1/\sqrt{6})(1,1,2) . \tag{19}$$

Consider now the matrices of the permutations when represented in this basis. They are

$$T_{12}=\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} ,$$

$$T_{13}=\begin{bmatrix} \frac{1}{2} & \sqrt{3}/2 \\ \sqrt{3}/2 & -\frac{1}{2} \end{bmatrix} , \tag{20}$$

$$T_{23}=\begin{bmatrix} \frac{1}{2} & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -\frac{1}{2} \end{bmatrix} ,$$

and a basis of the space that they generate is

$$M_2=\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad M_3=\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} . \tag{21}$$

The identity permutation generates a one-dimensional subspace supplementer to the previous one, and is represented by

$$M_1=\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} . \tag{22}$$

These three matrices generate a basis of the vectorial space of quadratic forms through the relation

$$\begin{bmatrix} X_1 \\ X_2 \end{bmatrix} \rightarrow A_i(X)=(X_1 \quad X_2)\cdot M_i\otimes I_3\cdot \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} . \tag{23}$$

The coordinates that are obtained are given by

$$\begin{aligned} A_1(X)&=X_1^2+X_2^2 , \\ A_2(X)&=X_1^2-X_2^2 , \\ A_3(X)&=2X_1\cdot X_2 . \end{aligned} \tag{24}$$

(A_1,A_2,A_3) therefore form a system of coordinates for the configuration space divided by rotations and translations. Notice that these coordinates are bound by the triangular inequality which imposes that

$$A_1^2(X) > A_2^2(X)+A_3^2(X) . \tag{25}$$

These coordinates can now be used to divide further by permutations and generate a proper system of coordinates. The first step to accomplish this is to look at the action of the permutation group on these quadratic forms, so that the division by permutations appears as a restriction to a subset of the space that they span. This can be done by looking at the action of transpositions, since they generate the whole permutation group.

It is then seen that the transpositions leave A_1 invariant so that permutations can be understood through their action on the plane generated by A_2 and A_3. With these conventions, their action can be represented in the basis (A_2,A_3) by the matrices

$$\tau_{12}: \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} ,$$

$$\tau_{13}: \begin{bmatrix} -\frac{1}{2} & \sqrt{3}/2 \\ \sqrt{3}/2 & \frac{1}{2} \end{bmatrix} ,$$

$$\tau_{23}: \begin{bmatrix} -\frac{1}{2} & -\sqrt{3}/2 \\ -\sqrt{3}/2 & \frac{1}{2} \end{bmatrix} .$$

Thus, for example, the configurations defined by (A_1,A_2,A_3) and $(A_1,A_2,-A_3)$ are symmetry related (through τ_{12}), and those such that $A_3=0$ are symmetry configurations (they are in fact isosceles triangles where atoms 1 and 2 can be exchanged). The two other transitions act in a similar fashion as inversions with respect to planes constructed on the vectors:

$$((0,1,\sqrt{3}),(1,0,0)) \quad \text{for } \tau_{13} ,$$

and

$$((0,1,-\sqrt{3}),(1,0,0)) \quad \text{for } \tau_{23} .$$

The configuration space will therefore be divided by permutations if A_2 and $\sqrt{3}A_2+A_3$ are restricted to be positive (which implies that $\sqrt{3}A_2-A_3$ is positive). The reduced space appears as the intersection between a cone [defined by inequality (25)] and a dihedral with a basis delimited by the directions $A_3=0$ and $\sqrt{3}A_2=A_3$ (see Fig. 2). Each of the lateral faces of the dihedral represents isosceles triangles and the axis A_1 represents equilateral triangles. The surface of the cone, which is the other limit, represents degenerate triangles (the three atoms form a line).

At this point there are two different ways to proceed. One is to apply the scheme introduced in Sec. IV. The other is more geometrical than algebraic. It consists of defining three families of surfaces ($f_1=K_1$, $f_2=K_2$, $f_3=K_3$), each being invariant under the action of the group, such that their intersection defines symmetry-related points. As this second option was the first to be developed and used, and as the result it gives is

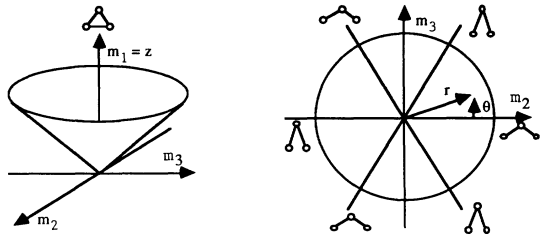


FIG. 2. Schematic of the three-body configuration space. The figure on the left represents the full three-body configuration space which is limited to the interior of the cone. The z axis represents equilateral configurations. The isosceles configurations are represented in the (r,q) plane (right-hand figure). The division by permutations can be viewed as a restriction to one of the dihedrals delimited by the planes of isosceles triangles.

equivalent to that obtained from the first method, it is the one that is presented here. It will be seen that in the case of four atoms a geometrical method such as this is not efficient (mainly due to the fact that it is difficult to imagine families of surfaces in six dimensions). The algebraic scheme will therefore be used to circumvent this difficulty. Even so, an attempt will be made to recover some geometrical insight in constructing the final coordinates.

Consider first the spherical coordinates (r,θ,φ) that will be used further to construct invariants. Thus, consider

$$r^2=A_1^2(X)+A_2^2(X)+A_3^2(X)$$
$$=(X_1^2+X_2^2)^2+(X_1^2-X_2^2)^2+(2X_1\cdot X_2)^2\ , \tag{26}$$

$$\cos\theta=\frac{A_2(X)}{[A_2^2(X)+A_3^2(X)]^{1/2}}$$
$$=\frac{X_1^2-X_2^2}{[(X_1^2-X_2^2)^2+(2X_1\cdot X_2)^2]^{1/2}}\ ,$$
$$\sin\theta=\frac{A_3(X)}{[A_2^2(X)+A_3^2(X)]^{1/2}} \tag{27}$$
$$=\frac{2X_1\cdot X_2}{[(X_1^2-X_2^2)^2+(2X_1\cdot X_2)^2]^{1/2}}\ ,$$

$$\sin\varphi=\frac{\{[A_2(X)]^2+[A_3(X)]^2\}^{1/2}}{r}$$
$$=\frac{[(X_1^2-X_2^2)^2+(2X_1\cdot X_2)^2]^{1/2}}{[(X_1^2+X_2^2)^2+(X_1^2-X_2^2)^2+(2X_1\cdot X_2)^2]^{1/2}}\ , \tag{28}$$
$$\cos\varphi=\frac{A_1(X)}{r}$$
$$=\frac{X_1^2+X_2^2}{[(X_1^2+X_2^2)^2+(X_1^2-X_2^2)^2+(2X_1\cdot X_2)^2]^{1/2}}\ .$$

Notice that r and φ are invariant and that the action of the group can be represented on θ by symmetries around 0, $\pi/3$, and $2\pi/3$. Moreover, there are boundary conditions on the limits of the sector of cone of interest that will be taken care of if the following coordinates are considered:

$$(r,s_1,s_2)=(r,\sin^2(3\theta/2),\sin(2\varphi))\ , \tag{29}$$

which can be expressed as

$$\sin^2(3\theta/2)=\tfrac{1}{2}\{1-\cos\theta[4\cos^2\theta-3]\}\ , \tag{30}$$

where $\cos\theta$ is given above and

$$\sin(2\varphi)=2\sin\varphi\cos\varphi\ , \tag{31}$$

where $\sin\varphi$ and $\cos\varphi$ are also given above.

The above coordinates form a proper system of coordinates, as can be checked by solving for the A's (an equation of degree 6 is obtained which has indeed six real roots). The four-body coordinates are now presented, which are a direct application of the scheme described in Sec. IV and could not have been constructed without it.

VII. FOUR-BODY COORDINATES

A. From atomic coordinates to invariant polynomials

As in the case $p=3$, a change of basis is made to separate the global translations:

$$\begin{bmatrix}u_1\\u_2\\u_3\\u_4\end{bmatrix}\rightarrow\begin{bmatrix}X_0\\X_1\\X_2\\X_3\end{bmatrix}=\begin{bmatrix}\frac{1}{2}(u_1+u_2+u_3+u_4)\\\frac{1}{2}(u_1-u_2+u_3-u_4)\\\frac{1}{2}(u_1-u_2-u_3+u_4)\\\frac{1}{2}(u_1+u_2-u_3-u_4)\end{bmatrix}\ . \tag{32}$$

The space $F\otimes\mathbb{R}^3$ is then spanned by the tensors $X=(X_1,X_2,X_3)$ and F itself is spanned by the vectors

$$e_1=\tfrac{1}{2}(1,-1,1,-1)\ ,$$
$$e_2=\tfrac{1}{2}(1,-1,-1,1)\ , \tag{33}$$
$$e_3=\tfrac{1}{2}(1,1,-1,-1)\ .$$

Consider now the matrices of the permutations when represented in this basis. They are

TABLE I. Action of transpositions on quadratic forms, first basis.

$t_{\tau\cdot T\cdot\tau}$	τ_{12}	τ_{13}	τ_{14}	τ_{23}	τ_{24}	τ_{34}
T_{12}	T_{12}	T_{23}	T_{24}	T_{13}	T_{14}	T_{12}
T_{13}	T_{23}	T_{13}	T_{34}	T_{12}	T_{13}	T_{14}
T_{14}	T_{24}	T_{34}	T_{14}	T_{14}	T_{12}	T_{13}
T_{23}	T_{13}	T_{12}	T_{23}	T_{23}	T_{34}	T_{24}
T_{24}	T_{14}	T_{24}	T_{12}	T_{34}	T_{24}	T_{23}
T_{34}	T_{34}	T_{14}	T_{13}	T_{24}	T_{23}	T_{34}

$$T_{12}=\begin{bmatrix}0&-1&0\\-1&0&0\\0&0&1\end{bmatrix},\quad T_{13}=\begin{bmatrix}1&0&0\\0&0&-1\\0&-1&0\end{bmatrix},\quad T_{14}=\begin{bmatrix}0&0&-1\\0&1&0\\-1&0&0\end{bmatrix},$$
$$T_{34}=\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix},\quad T_{24}=\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix},\quad T_{23}=\begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}, \tag{34}$$

and they form a basis of the space of symmetric matrices. The action of the transpositions is summarized in Table I.

The change of basis (in the space of quadratic forms),

$$A_1=\tfrac{1}{4}(T_{24}-T_{13})=\frac{1}{2}\begin{bmatrix}0&0&0\\0&0&1\\0&1&0\end{bmatrix},$$
$$A_2=\tfrac{1}{2}(T_{24}+T_{13})=\begin{bmatrix}1&0&0\\0&0&0\\0&0&0\end{bmatrix},$$
$$B_1=\tfrac{1}{4}(T_{23}-T_{14})=\frac{1}{2}\begin{bmatrix}0&0&1\\0&0&0\\1&0&0\end{bmatrix},$$
$$B_2=\tfrac{1}{2}(T_{23}+T_{14})=\begin{bmatrix}0&0&0\\0&1&0\\0&0&0\end{bmatrix}, \tag{35}$$
$$C_1=\tfrac{1}{4}(T_{12}-T_{34})=\frac{1}{2}\begin{bmatrix}0&1&0\\1&0&0\\0&0&0\end{bmatrix},$$
$$C_2=\tfrac{1}{2}(T_{12}+T_{34})=\begin{bmatrix}0&0&0\\0&0&0\\0&0&1\end{bmatrix},$$

allows the action of transpositions to be rewritten in the form shown in Table II.

There are two consequences. First, it is seen that permutations do not mix A_1,B_1,C_1 and A_2,B_2,C_2 (since the transpositions listed above generate the whole permutation group). What is obtained here is the decomposition of a six-dimensional representation into two three-dimensional ones. It can be seen further that one of these representations is irreducible (the one spanned by A_1, B_1, and C_1) and that the other breaks into a one-dimensional and a two-dimensional representation [consider, in the space spanned by A_2, B_2, and C_2, the space generated by (1,1,1) and its orthogonal space]. Hence, the action of permutations can be viewed in $\mathbb{R}^3\times\mathbb{R}^3$. The action of permutations in that space can therefore be listed which permits the division by permutations to be viewed through a restriction to a sector of the total space, in a manner similar to the case of three atoms. However, constructing coordinate systems will require that the A_1's and the A_2's are mixed so that the kind of geometrical construction developed for three atoms cannot be used.

Second, the actions of permutations on the A's can be listed so that invariant polynomials can be constructed in the same way Demazure[8] has done with the q_{ij}'s. Eight polynomials are obtained that are equivalent to the eight first graphs of Demazure.[8] The first eight invariants are

TABLE II. Action of transpositions on quadratic forms, second basis.

$t_{\tau\cdot T\cdot\tau}$	τ_{12}	τ_{13}	τ_{14}	τ_{23}	τ_{24}	τ_{34}
A_1	A_1	$-C_1$	$-B_1$	B_1	C_1	A_1
B_1	$-C_1$	B_1	$-A_1$	A_1	B_1	C_1
C_1	$-B_1$	$-A_1$	C_1	C_1	A_1	B_1
A_2	A_2	C_2	B_2	B_2	C_2	A_2
B_2	C_2	B_2	A_2	A_2	B_2	C_2
C_2	B_2	A_2	C_2	C_2	A_2	B_2

listed below:

$$
\begin{aligned}
&r_1 = A_2 + B_2 + C_2, \quad r_5 = A_2 A_1^2 + B_2 B_1^2 + C_2 C_1^2 , \\
&r_2 = A_2^2 + B_2^2 + C_2^2, \quad r_6 = A_2^2 A_1^2 + B_2^2 B_1^2 + C_2^2 C_1^2 , \\
&r_3 = A_2 B_2 C_2, \quad r_7 = A_1 B_1 C_1 , \\
&r_4 = A_1^2 + B_1^2 + C_1^2, \quad r_8 = A_1^4 + B_1^4 + C_1^4 .
\end{aligned} \tag{36}
$$

B. Geometrical approach to the reduced space

As mentioned above, the division by permutations in the space $\mathbb{R}^3 \times \mathbb{R}^3$ spanned by A_1, B_1, C_1, A_2, B_2, and C_2 can be viewed through a restriction to the subset of $\mathbb{R}^3 \times \mathbb{R}^3$ defined by the inequalities

$$
\begin{aligned}
&A_1 + B_1 > 0, \quad A_2 > B_2 , \\
&B_1 + C_1 > 0, \quad C_2 > A_2 , \\
&A_1 + C_1 > 0 .
\end{aligned} \tag{37}
$$

It is seen that the group operations transform this subset into other subsets which, together with the faces that separate them, form a partition of the total space. In this representation, the reduced space appears with faces and edges of decreasing dimensionality. The structure of these faces and edges turns out to be a good way to understand the total space, for the edges with the lowest dimensionality correspond to symmetry configurations. The edges with the lowest dimensionalities are therefore listed, which allows meaning to be attached to the points of that space. It is in this way that the final coordinates chosen are understood. The final coordinates are seen as families of surfaces in that space which admit some of these edges as limiting cases. Hence, configurations with high symmetry appear as extrema of the coordinates.

It should also be noted that the A_1's and the A_2's are not totally independent. They are bound by triangular inequalities:

$$
\begin{aligned}
&A_1 < \sqrt{B_2 C_2} , \\
&B_1 < \sqrt{A_2 C_2} , \\
&C_1 < \sqrt{A_2 B_2} , \\
&A_2 A_1^2 + B_2 B_1^2 + C_2 C_1^2 - 2 A_1 B_1 C_1 < A_2 B_2 C_2 .
\end{aligned} \tag{38}
$$

Table III lists the most important limiting cases.

C. Obtaining a coordinate system

The difficulties related to the existence of coordinate systems are now presented. As shown by Demazure,[8] the seven first polynomials generate the field of rational fractions. Since the space of interest has dimension 6, it would be desirable to have only six coordinates. The first set of coordinates to examine consists of polynomials r_1, r_2, r_3, r_4, r_5, and r_7, since they are of lowest degree. To determine whether they form a coordinate system or not, an attempt is made to solve for the A's in terms of $r_1, \ldots, r_5, r_7$. If this can be done, then a solution can be found for the configuration itself, which would show that the corresponding configuration exists and is unique. Consider therefore the set of equations

$$
(i) \quad r_i = k_i , \tag{39}
$$

where i belongs to $\{1,2,3,4,5,7\}$ and $k_1, \ldots, k_5, k_7$ are

TABLE III. Symmetric four-body configurations expressed in the second basis of the space of quadratic forms.

Zero dimensional	
$A_2 = B_2 = C_2 = 0$	Four atoms in one point
One dimensional	
$A_2 = B_2 = C_2, \; A_1 = B_1 = C_1 = 0$	Regular tetrahedron
$A_2 = B_2, \; C_2 = 0, \; A_1 = B_1 = C_1 = 0$ or symmetry-related equations	Square
$A_2 = B_2 = C_2 = -2A_1 = -2B_1 = -2C_1$ or symmetry-related equations	Equilateral triangular star
$A_2 = B_2 = 0$ or symmetry-related equations	Degenerate: 2 points; 2+2
$A_2 = B_2 = C_2 = A_1 = -B_1 = -C_1$ or symmetry-related equations	Degenerate: 2 points; 3+1
Two dimensional	
$A_2 = B_2, \; A_1 = B_1 = C_1 = 0$ or symmetry-related equations	Distorted tetrahedron
$A_2 = 0, \; A_1 = B_1 = C_1 = 0,$ or symmetry related equations	Rectangle
$A_2 = B_2 = C_2, \; A_1 = B_1 = C_1$ or symmetry-related equations	Triangular pyramid

values taken by $r_1,\ldots,r_5,r_7$ (so that the system has at least six real solutions). In practice, at least as many solutions are obtained as there are permutations because the r_i are symmetric. What is required is that there exist no further solutions.

Consider first r_1,r_2,r_3. Then if

$$s_1=r_1,\quad s_2=\tfrac{1}{2}(r_1^2-r_2),\quad s_3=r_3\ , \tag{40}$$

then A_2,B_2,C_2 appear as the three roots of the polynomial

$$X^3-s_1X^2+s_2X-s_3\ .$$

The roots are therefore defined up to their relative order. Choosing an order, an attempt can be made to solve for A_1,B_1,C_1 using A_2,B_2,C_2,r_4,r_5,r_7.

The first difficulty appears here: if $A_2=B_2=C_2$, then the equations with $i=4$ and 5 are equivalent. It is therefore not possible to solve for A_1,B_1,C_1. This illustrates the existence of hypersurfaces on which the system of coordinates would not be efficient, as pointed out in the conclusion of Sec. IV.

Suppose that this is not the case. Then if $X=A_1^2$, $Y=B_1^2$, and $Z=C_1^2$, equations with $i=4$, 5, and 7 imply that

$$\begin{aligned}&(i=4)\quad X+Y+Z=k_4\ ,\\ &(i=5)\quad A_2X+B_2Y+C_2Z=k_5\ ,\\ &(i=7)\quad XYZ=k_7^2\ .\end{aligned} \tag{41}$$

The surface defined by $i=7$ cuts the plane defined by $i=4$ along a complicated curve. However, the interesting part of that curve (defined by $X>0$, $Y>0$, $Z>0$) is closed (and triangular looking). The plane defined by $i=5$ cuts $i=4$ along a line, which generally intersects the closed curve at two distinct points. These two points then generate two families of solutions which are not related by symmetry (one considers the roots of X, Y, and Z and selects the signs according to that of k_7).

In order to eliminate this degeneracy, another equation is needed. For example,

$$(i=6)\quad A_2^2X+B_2^2Y+C_2^2Z=k_6\ ; \tag{42}$$

then the point (X,Y,Z) appears as the intersection of three planes, which is a single point when A_2,B_2,C_2 are all different (the determinant of the linear system of equations with $i=4,5,6$ is a Vandermonde). This shows the following.

(a) The two solutions of the system with $i=4,5,7$ are not symmetry related, for they are discriminated by a symmetric polynomial.

(b) The polynomials $r_1,\ldots,r_5,r_7$ are not enough to define a proper coordinate system. At least seven coordinates have to be used to describe a dense set in the configuration space.

Now consider the problem in a more systematic way.

Case 1. Suppose that $A_2=B_2=C_2$. The rank of the system of equations with $i=4,5,6$ is then equal to 1. Consider the system

$$\begin{aligned}&(i=4)\quad r_4=k_4\ ,\\ &(i=7)\quad r_7=k_7\ ,\\ &(i=8)\quad r_8=k_8\ .\end{aligned} \tag{43}$$

It implies

$$\begin{aligned}&(i=4)\quad X+Y+Z=k_4\ ,\\ &(i=8)\quad X^2+Y^2+Z^2=k_8\ ,\\ &(i=7')\quad XYZ=k_7^2\ .\end{aligned} \tag{44}$$

This defines X,Y,Z up to relative order. It can then be checked that the roots of X,Y,Z that give the correct sign for r_7 are symmetry related. This shows that r_4, r_7, and r_8 are enough to obtain A_1,B_1,C_1 in this case.

Case 2. Suppose, for example, that $A_2=B_2$ and $A_2\neq C_2$. Then, the rank of the system $i=4,5,6$ is equal to 2. Consider the system

$$\begin{aligned}&(i=4)\quad r_4=k_4\ ,\\ &(i=5)\quad r_5=k_5\ ,\\ &(i=7)\quad r_7=k_7\ .\end{aligned} \tag{45}$$

It implies

$$\begin{aligned}&(i=4)\quad X+Y+Z=k_4\ ,\\ &(i=5)\quad A_2X+A_2Y+C_2Z=k_5\ ,\\ &(i=7')\quad XYZ=k_7^2\ ,\end{aligned} \tag{46}$$

from which $s_1=X+Y$, $s_2=XY$, and Z are easily computed. Hence, X and Y are obtained as the two roots x_1,x_2 of an equation of degree of 2. Two families of solutions are therefore obtained. They are given by the square roots of, respectively, (x_1,x_2,Z) and (x_2,x_1,Z), to which we give signs such that $r_7=k_7$. As $A_2=B_2$, these two families of solution are symmetry related. This shows that r_4, r_5, and r_6 are enough to obtain A_1, B_1, and C_1 in this case.

Case 3. Suppose that A_2, B_2, and C_2 are all distinct. This is the first case considered, and it was seen that r_4, r_5, r_6, and r_7 were needed to solve for A_1, B_1, and C_1.

All the previous results may be summarized as follows: (i) If $A_2=B_2=C_2$, then the six polynomials r_1, r_2, r_3, r_4, r_7, and r_8 can be used in order to describe a configuration without ambiguity; (ii) if $A_2=B_2\neq C_2$ (or if $A_2=C_2\neq B_2$, or $C_2=B_2\neq A_2$), then the six polynomials r_1, r_2, r_3, r_4, r_5, and r_7 have to be used; and (iii) if neither of the previous conditions hold, then the seven polynomials r_1, r_2, r_3, r_4, r_5, r_6, and r_7 have to be used.

An equivalent and more concise way of stating the same thing is to say that any symmetric function defined on the configuration space can be written as

$$\begin{aligned}f(u_1,u_2,u_3,u_4)=&\,f_1(r_1,r_2,r_3,r_4,r_7,r_8)+g_2(A_2,B_2,C_2)f_2(r_1,r_2,r_3,r_4,r_5,r_7)\\ &+g_3(A_2,B_2,C_2)f_3(r_1,r_2,r_3,r_4,r_5,r_6,r_7)\ ,\end{aligned} \tag{47}$$

where f_1, f_2, f_3 are general functions and g_2 and g_3 are functions such as

$$g_2(A_2,B_2,C_2)=(A_2-B_2)^2(B_2-C_2)^2(C_2-A_2)^2 , \tag{48}$$

$$g_3(A_2,B_2,C_2)=(A_2-B_2)^2(B_2-C_2)^2+(A_2-B_2)^2(C_2-A_2)^2+(C_2-A_2)^2(B_2-C_2)^2 . \tag{49}$$

In order to choose the functions f_1, f_2, f_3 more conveniently, a change of coordinates is made such that all but one of the coordinates are bounded. The unbounded coordinate may then be thought of as a radius, whereas the others can be thought of as "angular" coordinates. The final coordinates include the symmetry elements listed in Table III as limiting cases, so that the symmetry configurations have simple equations in this coordinate system.

Taking into account the triangular inequalities, a good choice of coordinates seems to be

$$\begin{aligned} &x_1=\sqrt{r_2},\quad x_4=[r_7^2-(r_4/3)^3]/r_2^3,\quad x_7=r_7/(r_2)^{3/2} ,\\ &x_2=(r_1/\sqrt{r_2})-\sqrt{3},\quad x_5=r_4(r_5-2r_7-r_3)/(r_2)^{5/2},\quad x_8=r_8/r_2^2 ,\\ &x_3=(r_3/(r_2)^{3/2})-1/3\sqrt{3},\quad x_6=r_6/r_2^2 . \end{aligned} \tag{50}$$

We see the following.

(a) x_1 is positive and varies quadratically with respect to interatomic distances. It is the only coordinate which is not bounded, and can therefore be thought of as a radius in the configuration space. The other coordinates are seen to define the geometry of the configuration. Notice further the following.

(b) x_2 is negative and equal to zero when $A_2=B_2=C_2$.

(c) x_3 is negative and equal to zero when $A_2=B_2=C_2$.

(d) x_4 is negative and equal to zero when $|A_1|=|B_1|=|C_1|$.

(e) x_5 is negative and equal to zero when the configuration is planar.

Presented below are the equations of some interesting symmetry configurations. They are represented in Fig. 3.

Tetrahedron	$x_2=x_3=x_4=x_6=x_7=0$
Triangular pyramid	$x_2=x_3=x_4=0$
Triangular star	$x_2=x_3=x_4=x_5=0.$

VIII. CONCLUSIONS

The problem of understanding the morphology of local potentials is addressed for the case of three- and four-body terms. Coordinate systems in the configuration spaces of three and four atoms are constructed that allow for the analysis of these spaces in terms of their symmetry configurations. The use of these coordinate systems then permits the local potential morphology to be chosen. For the case of three atoms, coordinates are constructed on a reduced configuration space which is restricted to a regular dihedral with well-defined faces, edges, and corners. For four atoms, the coordinates are expressed in terms of Demazure's polynomials on a reduced space that exhibits singularities. These coordinates enable some specific singularities, which are important symmetry configurations, to be understood. Applications of these coordinate systems include the construction of many-body interatomic potentials (see companion paper[4]) and the analysis of the local geometry around an atom in a crystal.

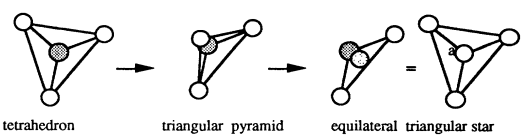


FIG. 3. Symmetrical four-body configurations. The triangular pyramid is seen as an intermediate configuration between the two others. The shaded atoms lie in a plane below the other atoms.

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APPENDIX

This appendix shows that in the case of four atoms, a generating family of the subalgebra of polynomials invariant under atomic permutations includes at least seven elements.

S_4 and the octahedron group

Let M be a set with four elements and Q be the set of all subsets of M with two elements. Then the group $\mathcal{S}_M$ of all 24 permutations of M acts on Q, defining a subgroup $\mathcal{S}_M$ of the group $\mathcal{S}_Q$ of all 720 permutations of Q. Q is made a graph by joining two subsets A and B by a edge when $A \cap B$ has exactly one element. Then each element of Q is connected to all others except exactly one (its complement in A), and the graph Q is an octahedron. The eight triangular faces of this octahedron are of two kinds: one, say, the white ones, are the four triangles of the form $\{ab,ac,ad\}$, where a is a point of M and b,c,d the three others; the four others, of the form $\{bc,cd,db\}$ are the black ones. Note that white and black triangles are 2×2 opposites (nonintersecting) and that each pair of opposed triangles can be labeled by an element of M (a in the case above).

The subgroup $\mathcal{O}$ of $\mathcal{S}_Q$ made by the automorphisms of this octahedron has 48 elements and is exactly the normalizer of $\mathcal{S}_M$ in $\mathcal{S}_Q$. Moreover, $\mathcal{O}$ is a maximal subgroup of $\mathcal{S}_Q$ and $\mathcal{S}_M$ is the subgroup of index 2 of $\mathcal{O}$ made of the automorphisms preserving the colors of the faces.

It can also be noted that all the elements of $\mathcal{S}_M$ are *even* permutations of Q and that $\mathcal{O}$ contains even and odd elements, the even ones being those of $\mathcal{S}_M$.

The appearance of this larger normalizer can also be explained in the following way. Given a set Q of six points, to give them the structure of an octahedron is equivalent to dividing them in three pairs of opposite points, and connecting nonopposite points. This can be done in $15=\frac{720}{48}$ ways. One such way having been chosen, there are 48 permutations of Q which respect the given decomposition in three pairs, and there are exactly two possibilities of alternately assigning white and black colors to the eight triangular faces. This assignment being fixed, each vertex belongs to exactly two white faces, and this labels the vertices by the two-element subsets of the four-element set of white faces.

The structure of $\mathcal{O}$

To fix notations, let 1, 2, 3, and 4 be the elements of M, so that the six elements of Q are 12, 13, 14, 23, 24, and 34, where ij denotes $\{i,j\}$. The opposite pairs are (12,34), (13,24), and (14,23).

The structure of $\mathcal{O}$ is very simple. It contains an Abelian subgroup H isomorphic to $(\mathbb{Z}/2\mathbb{Z})^3$, consisting of all automorphisms respecting each opposite pair, and it is the semidirect product of this invariant subgroup by the symmetric group $\mathcal{S}_3$ of all the six permutations of these three pairs.

Invariants of $\mathcal{S}_Q$

Consider the algebra of polynomials with rational coefficients in six variables X_{ij}, with $ij=\{i,j\}\in Q$:

$$P=\mathbb{Q}[X_{12},X_{13},X_{14},X_{23},X_{24},X_{34}]\ .$$

Then the group $\mathcal{S}_Q$ and its subgroups $\mathcal{O}$ and $\mathcal{S}_M$ act on P. The ring of invariants of the larger group $\mathcal{S}_Q$ is the polynomial algebra Σ generated by the classical elementary functions of the X's. Applying the notations used in this paper for the ten basic invariants of $\mathcal{S}_M$ associated to the simple graphs on four vertices, these six elementary functions are

$$s,t+u,v+w+n,y+z,r,p\ .$$

Invariants and anti-invariants of $\mathcal{O}$

The invariant ring of H is the polynomial ring in the six variables:

$$A_1=X_{12}+X_{34},\quad B_1=X_{12}X_{34}\ ,$$
$$A_2=X_{13}+X_{24},\quad B_2=X_{13}X_{24}\ ,$$
$$A_3=X_{14}+X_{23},\quad B_3=X_{14}X_{23}\ .$$

The group $\mathcal{S}_3$ acts by permutation on the A's and the B's, and its invariant ring ("bisymmetric functions"; see below) is the invariant ring of $\mathcal{O}$ in P. The invariant ring of $\mathcal{S}_M$ is a super-ring of the latter which has twice as many elements.

The ten basic invariants of $\mathcal{S}_M$ correspond to sums extended to certain configuration of nodes of the octahedron. Eight of them are invariant under $\mathcal{O}$, the two remaining ones being v and w which correspond to sums extended to triangular faces, and come in two "colored" versions. Hence, $v+w$ and vw are invariant under $\mathcal{O}$. To simplify, write $k=v+w$, which with the other eight gives us nine basic invariants for $\mathcal{O}$. Actually, vw can be expressed as a polynomial in these nine basic invariants because of the relation

$$vw=-(v+w)n-\tfrac{4}{3}tu^2+\tfrac{4}{3}sun-\tfrac{4}{3}n^2-\tfrac{4}{3}s^2y$$
$$+\tfrac{16}{3}ty+tz+\tfrac{4}{3}uz-\tfrac{8}{3}sr+16p\ .$$

The element $v-w$ in *anti-invariant* under $\mathcal{O}$: it transforms under an element of $\mathcal{O}$ in $v-w$ or $w-v$, according to the signature of this element (as a permutation of Q).

Lemma. Any anti-invariant a of $\mathcal{O}$ is divisible by $v-w$ in the ring P; hence, a can be expressed as $(v-w)b$, where b is an invariant of $\mathcal{O}$.

Proof. The transposition of X_{12} and X_{34} is an element of $\mathcal{O}$. Under it, a changes sign. This implies that a is divisible in P by $X_{12}-X_{34}$. By the same argument, it is divisible by $X_{13}-X_{24}$ and $X_{14}-X_{23}$. But a trivial calculation gives

$$(X_{12}-X_{34})(X_{13}-X_{24})(X_{14}-X_{23})=v-w\ .$$

Invariants of $\mathcal{S}_M$ and invariants of $\mathcal{O}$

Proposition. Any invariant a of $\mathcal{S}_M$ can be expressed in a unique way as $a=c+bv$, where b and c are invariants of $\mathcal{O}$.

Proof. Let a be an invariant of $\mathcal{S}_M$. Then, under all elements of $\mathcal{O}$ not in $\mathcal{S}_M$, a becomes a certain element a', also invariant under $\mathcal{S}_M$. Also, $a+a'$ is invariant under $\mathcal{O}$ and $a-a'$ is anti-invariant. By the preceding lemma, there exists an invariant b of $\mathcal{O}$ with $a-a'=(v-w)b$. But this gives $a-vb=a'-wb$, so that $c=a-vb$ is invariant under $\mathcal{O}$. This gives $a=c+bv$, as claimed. Unicity is obvious because, from $a=c+bv$, one deduces $a'=c+bw$; hence, $b(v-w)=a-a'$.

This proposition means that the ring of invariants of $\mathcal{S}_M$ is obtained from the ring of invariants of $\mathcal{O}$ as the quadratic extension associated to the quadratic polynomial

$$(X-v)(X-w)=X^2-kX+(-kn+\cdots+16p)\ .$$

Bisymmetric functions

Consider now the determination of the ring of invariants of $\mathcal{O}$. More generally, consider a polynomial ring in two sets of r variables,

$$R=\mathbb{Q}[A_1,\ldots,A_r,B_1,\ldots,B_r],$$

and the action of the symmetric group $\mathcal{S}_r$ on it. The invariants of this action are by definition the *bisymmetric functions*. Call *elementary bisymmetric functions* the elements obtained by bisymmetrization of the monomials of the form

$$m_{s,t}=A_1\cdots A_sB_{s+1}\cdots B_{s+t},\qquad 0\le s,\quad 0\le t,\quad 1\le s+t\le r,$$

say, $\sigma_{s,t}$. For instance, the $\sigma_{s,0}$ are the elementary symmetric functions of the A's, and the $\sigma_{0,t}$ are the elementary symmetric functions of the B's. Altogether, there are $r(r+3)/2$ such elementary bisymmetric functions.

Proposition. (a) The $\sigma_{s,t}$ generate the algebra of all bisymmetric functions: Every bisymmetric function can be written as a polynomial with rational coefficients in the $\sigma_{s,t}$. (b) Every bisymmetric function can be written (in a unique way) as a rational fraction with rational coefficients in the $2r$ elements $\sigma_{s,0}$ for $s=1,\ldots,r$ and $\sigma_{s,1}$ for $s=0,\ldots,r-1$.

Proof. The proof of (a) can be found in Bourbaki.[10] The proof of (b) is a simple application of Galois theory. To simplify the notations, we write $\sigma_s=\sigma_{s,0}$ and $\tau_s=\sigma_{s,1}$. Let us consider the four fields K, K', L, and L' defined as follows. K is generated by the σ_s and the τ_s, L is generated by the A_i and the τ_s, L' is generated by the A_i and the B_i, and K' is the field of invariants of $\mathcal{S}_r$ in L':

$$\begin{array}{ccc}\mathbb{Q}[(A_i),(\tau_s)]=L & \subset & L'=\mathbb{Q}[(A_i),(B_i)]\\ \cup & & \cup\\ K & \subset & K'=L'^{\text{invar}}.\end{array}$$

By construction,

$$\prod_{i=1}^{r}(X-A_i)=X^r-\sigma_1X^{r-1}+\cdots+(-1)^r\sigma_r$$

so that L has degree $\le r!$ (actually $=r!$) over K. By Galois, L' has degree $r!$ over K'. Suppose that $L=L'$; this will imply that L' has degree $\le r!$ over K, so that $K=K'$ and the field of invariants is generated by the σ's and the τ's. Moreover, because L' has transcendence degree $2r$, so has K', and K' is the field of rational fractions in this $2r$ generator.

The claim to be proven means that the B_i can be computed as rational fractions of the A_i and the τ_s. But there is by definition a linear system,

$$B_1+\cdots+B_r=\tau_0,$$

$$B_1(A_2+\cdots+A_r)+\cdots+B_r(A_1+\cdots+A_{r-1})=\tau_1,$$

$$\cdots=\cdots,$$

$$B_1A_2\cdots A_r+\cdots+B_rA_1\cdots A_{r-1}=\tau_{r-1},$$

whose determinant is readily seen to be the Vandermonde determinant of the A_i (hence the square root of the discriminant of the equation above with the σ_s as coefficients). This ends the proof.

Invariants of $\mathcal{O}$

Take now $r=3$, coming back to the present case, and compute the nine elementary bisymmetric functions. We find the following:

$$\sigma_{1,0}=A_1+\cdots=(X_{12}+X_{34})+\cdots=s,$$

$$\sigma_{2,0}=A_1A_2+\cdots=(X_{12}+X_{34})(X_{13}+X_{24})+\cdots=t,$$

$$\sigma_{3,0}=A_1A_2A_3=(X_{12}+X_{34})(X_{13}+X_{24})(X_{14}+X_{23})=v+w=k,$$

$$\sigma_{0,1}=B_1+\cdots=X_{12}X_{34}+\cdots=u,$$

$$\sigma_{0,2}=B_1B_2+\cdots=X_{12}X_{34}X_{13}X_{24}+\cdots=y,$$

$$\sigma_{0,3}=B_1B_2B_3=X_{12}X_{34}X_{13}X_{24}X_{14}X_{23}=p,$$

$$\sigma_{1,1}=A_1B_2+\cdots=(X_{12}+X_{34})X_{13}X_{24}+\cdots=n,$$

$$\sigma_{2,1}=A_1A_2B_3+\cdots=(X_{12}+X_{34})(X_{13}+X_{24})X_{14}X_{23}+\cdots=z,$$

$$\sigma_{1,2}=A_1B_2B_3+\cdots=(X_{12}+X_{34})X_{13}X_{24}X_{14}X_{23}+\cdots=r.$$

Hence, we have the following proposition.

Proposition. (a) Every invariant of $\mathcal{O}$ can be expressed as a polynomial with rational coefficients in the nine invariants s,t,u,k,n,y,z,r,p, of respective degrees 1,2,2,3,3,4,4,5,6. (b) Every invariant of $\mathcal{O}$ can be expressed in a unique way as a rational fraction with rational coefficients in the six invariants s,t,u,k,n,z of respective degrees 1,2,2,3,3,4. (c) Every invariant of $\mathcal{O}$ can be expressed in a unique way as a rational fraction with rational coefficients in the six invariants s,u,n,y,r,p of respective degrees 1,2,3,4,5,6.

The expression given above for vw can be found either by brute force or by the following remark. Consider

$$(v-w)^2=(X_{12}-X_{34})^2(X_{13}-X_{24})^2(X_{23}-X_{14})^2,$$

but

$$(X_{12}-X_{34})^2=(X_{12}+X_{34})^2-4X_{12}X_{34}=A_1^2-4B_1,$$

which gives

$$(v-w)^2=(A_1^2-4B_1)(A_2^2-4B_2)(A_2^2-4B_2).$$

Then one uses the classical computations to reduce the bisymmetric functions to the elementary ones.

Invariants of $\mathcal{S}_M$

From the preceding we have the following.

Theorem. (a) Every invariant of $\mathcal{S}_4$ can be expressed as a polynomial with rational coefficients in the ten basic invariants s,t,u,v,w,n,y,z,r,p of respective degrees 1,2,2,3,3,3,4,4,5,6. (b) The field of invariants of $\mathcal{S}_4$ is generated by the seven basic invariants s,u,t,v,w,n,z of respective degrees 1,2,2,3,3,3,4,4 subject to a unique relation. In (a), the nine first invariants actually suffice, because the above-mentioned relation expresses p as a polynomial in them.

The relation

Using the Macaulay computer algebra system designed by Bayer,[11] an expression for R of degree 24 is obtained the details of which are given by Dallot.[12]

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