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Perimetric scale-shape coordinates for triatomic molecules

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Abstract Perimetric nuclear coordinates of a triatomic molecule treat all three nuclei equivalently and are not subject to the triangle conditions. Through an appropriate orthogonal transformation they can be separated into one scale coordinate, viz., the circumference, and two shape coordinates, which are determined by the angles. The parameter space of the shape coordinates is an equilateral triangle. The basic formulas are given and the relationship between points in coordinate space and molecular shapes are elucidated.

Key words Internal coordinates – Triatomic molecules

1 Introduction

Many features of polyatomic potential energy surfaces (PES) do not appear in the paradigm of diatomic potential energy curves. Moreover, because of our inability to "see" in more than three dimensions, their visualization is difficult. Triatomic molecules, being the smallest molecules with multidimensional PES, represent the necessary next step in understanding PES depending on more than one internal coordinate. They have three internal coordinates and furnish the simplest material on which to study, and become familiar with, features of general PES. Even in this case, however, an effort is required in order to relate the points in the internal coordinate space to the actual molecular shapes. We encountered this problem in the accompanying study of ozone [1], which led to the account presented below.

In discussions of triatomic molecules, it is desirable to be able to express and visualize PES or other properties as functions of the three internal coordinates in a way that treats all three atoms on an equal footing. Hyperspherical coordinate systems [2–4] meet this requirement, but these mass-dependent coordinates are not easily related to the geometric shape of the molecules they describe. A simpler parametrization which treats all three atoms symmetrically is given by the so-called perimetric coordinates. These were introduced in quantum chemistry by James and Coolidge [5] in the 1930s and used later by Pekeris [6], in both instances for electronic calculations on the He atom. Davidson [7] seems to have been the first to use and discuss perimetric coordinates for nuclear coordinates of triatomics. In the present note we examine this parametrization, establish its connection with Murrell's symmetry coordinates [8], separate the coordinates into scale and shape components, and illustrate the relationships between points in parameter space and molecular geometries.

2 Perimetric coordinates

2.1 Definition

The three distances r_{12}, r_{23}, r_{13}, between the nuclei N_1, N_2, N_3 are the most natural independent coordinates that treat the three nuclei equivalently, but they have the drawback of being subject to the triangle conditions $r_{ij} + r_{jk} \leq r_{ik}$. This shortcoming is eliminated by the perimetric coordinates defined as

$$s_i = (r_{ij} + r_{ik} - r_{jk})/2, \tag{1}$$

where (i, j, k) represents any permutation of $(1, 2, 3)$. Inversion of Eq. (1) yields

$$s_i + s_j = r_{ij}, \tag{2}$$

and Eqs. (1) and (2) are equivalent to the equations

$$s_i + r_{jk} = s = r/2, \tag{3}$$

where

$$s = (s_1 + s_2 + s_3), \tag{4}$$

$$r = (r_{12} + r_{23} + r_{13}). \tag{5}$$

The geometric meanings of s_1, s_2, s_3 are illustrated by Fig. 1, which is self-evident in view of Eq. (2). The points which separate the two segments s_i and s_j on the side r_{ij} are, in fact, the points where the inscribed circle touches the three sides of the molecular triangle [9]. The lines connecting the corners to the center of the inscribed circle bisect the respective angles.

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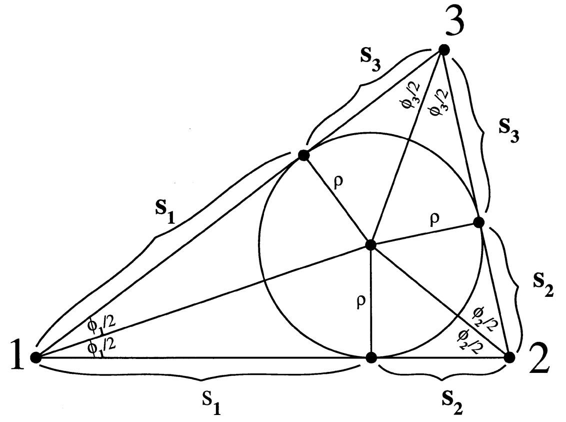


Fig. 1. Geometric meaning of the perimetric coordinates s_1, s_2, s_3

2.2 Scale and shape

The relation of the lengths s_i and r_{ij} to the angles can be derived from the formula

$$r_{ij} = 2\mathrm{R}\ \sin\phi_k, \tag{6}$$

where R is the radius of the *circumscribed* circle [9]. From Eq. (6) follows

$$r_{ij}/r = \sin\phi_k / \sum_l \sin\phi_l \tag{7}$$

and

$$s_i = sf_i \tag{8}$$

with

$$f_i = f_i(\phi_1, \phi_2, \phi_3) = 1 - 2\sin\phi_i / \sum_k \sin\phi_k. \tag{9}$$

Manifestly,

$$\sum_i f_i = 1. \tag{10}$$

It is apparent that, in Eq. (8), the parameter s determines the overall size of the molecule; it is a *scale factor*. The angular functions $f_i(\phi_1, \phi_2, \phi_3)$, on the other hand, determine the angular appearance of the molecule; they are *shape factors*. By virtue of the relation $\phi_1 + \phi_2 + \phi_3 = \pi$, the right-hand side of Eq. (9) can be recast in the form

$$f_i = \tan\frac{1}{2}\phi_j \cdot \tan\frac{1}{2}\phi_k. \tag{11}$$

2.3 Parameter space

Let the parameter space be spanned by a Cartesian axis system along which the (s_1, s_2, s_3) are taken as coordinates. Since the three perimetric coordinates vary independently from zero to infinity, only the first octant is used. In this parameter space, molecules *of the same angular shape* are given by the coordinates of Eq. (8) with *constant factors* f_i, i.e. by points which fall on straight rays through the origin, the internuclear distances being proportional to s.

The points along the diagonal of the first octant, for which $s_1 = s_2 = s_3$, correspond to equilateral molecules for which $f_1 = f_2 = f_3 = 1/3$.

Isosceles molecules correspond to points on the planes $s_i = s_j$; for example, the plane $s_1 = s_2$ contains all isosceles triangles with the nucleus N_3 at the apex.

The three coordinate planes $s_i = 0$ contains the points representing linear molecules. For example, the $s_1 - s_2$ plane, corresponding to $s_3 = 0$, contains the linear molecules with nucleus N_3 in between nuclei N_1 and N_2 and with the internuclear distances $r_{13} = s_1, r_{23} = s_2$, $r_{12} = r_{13} + r_{23} = s_1 + s_2$. Hence, all such linear molecules with $r_{12} =$ constant are located on a straight line which lies in the $s_3 = 0$ plane and intersects the s_1 as well as the s_2 axis at 45°.

The points on the three coordinate axes correspond to the coincidence of two nuclei. For example, the s_1 axis corresponds to $s_2 = s_3 = 0$ and the coincidence of nuclei N_2 and N_3, with $r_{12} = r_{13} = s_1$. The origin corresponds to the coincidence of all three nuclei.

3 Separation of scale and shape components

3.1 Rotation of coordinate basis

A separation of scale and shape coordinates is obtained by considering all molecules with a given circumference $r = 2s$. By virtue of Eq. (8) they are given by the points lying in the plane

$$s_1 + s_2 + s_3 = s = \text{constant}, \tag{12}$$

i.e. in a plane perpendicular to the diagonal of the first octant and intercepting all three axes at a distance $s = r/2$ from the origin. Accordingly, we introduce a new right-handed set of basis vectors $\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3$ by the orthogonal transformation

$$\begin{array}{c|ccc} & \mathbf{d}_1 & \mathbf{d}_2 & \mathbf{d}_3 \\ \hline \mathbf{e}_1 & -1/2 & -1/\sqrt{6} & 1/\sqrt{3} \\ \mathbf{e}_2 & 1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ \mathbf{e}_3 & 0 & 2/\sqrt{6} & 1/\sqrt{3}, \end{array} \tag{13}$$

where $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ denote the unit basis vectors along the axis s_1, s_2, s_3. Since $\mathbf{d}_3$ points along the first octant diagonal, the vectors $(\mathbf{d}_1, \mathbf{d}_2)$ span a plane passing through the origin and parallel to all planes $s =$ constant. The orientation of these basis vectors is shown in Fig. 2. If x_1, x_2, x_3 denote the new coordinates along the vectors $(\mathbf{d}_1, \mathbf{d}_2, \mathbf{d}_3)$, then

$$\sum_i \mathbf{e}_i s_i = \sum_k \mathbf{d}_k x_k, \tag{14}$$

and the transformation between (s_1, s_2, s_3) and (x_1, x_2, x_3) is given by the same orthogonal transformation:

$$\begin{array}{c|ccc} & x_1 & x_2 & x_3 \\ \hline s_1 & -1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ s_2 & 1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ s_3 & 0 & 2/\sqrt{6} & 1/\sqrt{3}. \end{array} \tag{15}$$

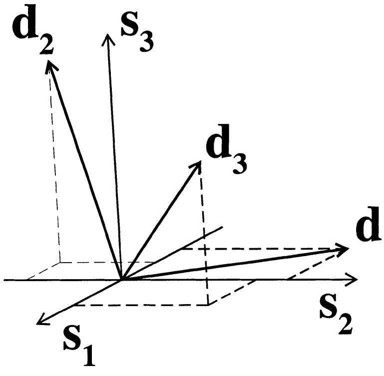


Fig. 2. Basis vectors for perimetric scale-shape coordinates

It entails

$$x_3 = (s_1 + s_2 + s_3)/\sqrt{3} = s/\sqrt{3} = r/\left(2\sqrt{3}\right), \tag{16}$$

confirming that the plane $s = \text{constant}$ is the plane $x_3 = \text{constant}$ and spanned by the coordinates (x_1, x_2).

Since the three-dimensional parameter space is limited to the first octant, the two-dimensional parameter plane for $x_3 = \text{constant}$ is limited to an equilateral triangle as illustrated, perspectively, in Fig. 3. The first octant diagonal penetrates this triangle in its origin $x_1 = x_2 = 0$ at a distance x_3 from the origin of the s_1, s_2, s_3 coordinate system. The coordinates (s_1, s_2, s_3) of a number of points on the triangle $s = \text{constant}$ are also given on Fig. 3. From these coordinates the dimensions of the triangle are found to be as follows: the origin lies two-thirds of the way from each corner to its opposite side, the side length is $s\sqrt{2}$, and the height is $s\sqrt{3/2}$. Figure 4 provides a plane view of this triangle with the coordinate axis x_1, x_2 on it. The corners are numbered by the axes s_1, s_2, s_3 penetrating the plane at those points.

In terms of the present coordinates, the symmetry coordinates, S_k, of Murrell [8] are given by $S_1 = 2x_3$, $S_2 = x_1$ and $S_3 = -x_2$.

3.2 Scale-independent shape coordinates

The *linear size* of the parameter triangle spanned by x_1, x_2 is proportional to the molecular scale parameter s. The *shape* of the molecule is given by the relative position of the representative point inside the triangle, i.e. by the two scale-independent parameters

$$\xi_1 = x_1/s, \ \xi_2 = x_2/s. \tag{17}$$

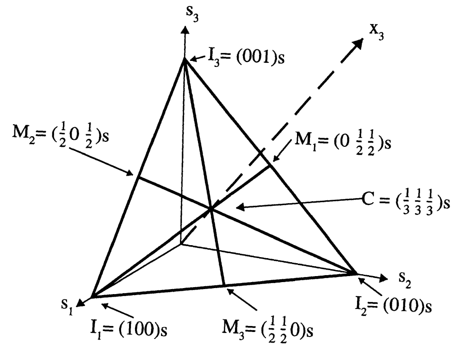


Fig. 3. Perspective view of two dimensional parameter plane for shape coordinates

These two independent shape coordinates are equivalent to the three angles ϕ_1, ϕ_2, ϕ_3, which are subject to the constraint $\phi_1 + \phi_2 + \phi_3 = \pi$. By virtue of the relations $s_i = sf_i$ [see Eq. (8)] and the orthogonal transformation, Eq.(15), between the x_i and the s_j, the two independent shape coordinates ξ_1, ξ_2 are related to the three dependent shape factors of Eqs.(9) and (11) by the orthogonal transformation

$$\begin{array}{c|ccc} & \xi_1 & \xi_2 & \xi_3 = 1/\sqrt{3} \\ \hline f_1 & -1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ f_2 & 1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ f_3 & 0 & 2/\sqrt{6} & 1/\sqrt{3}, \end{array} \tag{18}$$

where we formally introduced $\xi_3 = x_3/s = 1/\sqrt{3}$ [see Eq. (16)]. Manifestly, the parameter space of the scale-independent shape coordinates (ξ_1, ξ_2) also forms an equilateral triangle. The side of this triangle has a length of $\sqrt{2}$ and its height is $\sqrt{3/2} = 3/\sqrt{6}$.

From Eq.(18) one obtains for the s_i the following expression in terms of the independent scale-shape coordinates (s, ξ_i, ξ_2) :

$$\begin{aligned} s_1 &= s(-\xi_1/\sqrt{2} + \xi_2/\sqrt{6} + 1/3) \\ s_2 &= s(\xi_1/\sqrt{2} + \xi_2/\sqrt{6} + 1/3) \\ s_3 &= s(-2\xi_2/\sqrt{6} + 1/3), \end{aligned} \tag{19}$$

from which follows, by virtue of Eq.(2),

$$\begin{aligned} r_{13} &= s(-\xi_1/\sqrt{2} - \xi_2/\sqrt{6} + 2/3) \\ r_{23} &= s(\xi_1/\sqrt{2} - \xi_2/\sqrt{6} + 2/3) \\ r_{12} &= s(+2\xi_2/\sqrt{6} + 2/3). \end{aligned} \tag{20}$$

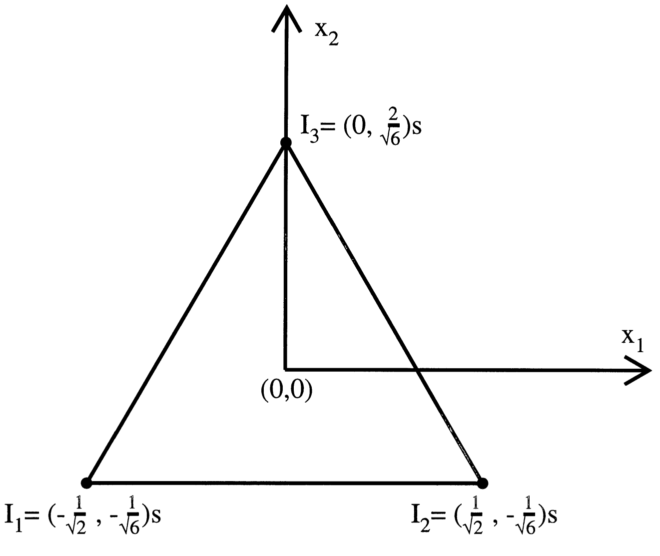


Fig. 4. Coordinates on parameter plane of the shape coordinates. The points I_1, I_2, I_3 are the same as those so labelled in Fig. 3

4 Relation between coordinate points and molecular shapes

4.1 General relationships

The visualization of molecules represented by arbitrary points in the triangle of the parameters x_1, x_2 is facilitated by the following theorem which is readily proved in the three-dimensional coordinate space of (s_1, s_2, s_3), depicted in Fig. 3:

The perpendicular distance D_j *between an arbitrary point in the parameter triangle and the side opposite to the corner j is related to the coordinate* s_j *by*

$$D_j = s_j\sqrt{3/2}. \qquad (21)$$

From it follows the corollary

$$\begin{aligned} D_1 + D_2 + D_3 &= s\sqrt{3/2} = \text{height of triangle} \\ &= \text{independent of shape}, \qquad (22) \end{aligned}$$

in agreement with a geometrical theorem about equilateral triangle. Figure 5 depicts the distances D_k as well as the distances D'_k to the *circumscribed equilateral triangle*. By virtue of Eq. (21), the latter distances D'_k are given by

$$\begin{aligned} D'_k &= (\text{height of original triangle}) - D_k = (s - s_k)\sqrt{3/2}, \\ &= (s_i + s_j)\sqrt{3/2} = r_{ij}\sqrt{3/2}. \qquad (23) \end{aligned}$$

It is easily seen that the limitation of the representative points to the original, shaded triangle in Fig. 5 is equivalent to the triangle conditions on the distance r_{ij}.

If $\delta_j = D_j/s$ denotes the distance corresponding to D_j in the triangle of the scale-independent shape coordinates (ξ_1, ξ_2), then they satisfy the corresponding identities

$$\delta_j = f_j\sqrt{3/2} \qquad (24)$$

and

$$\delta_1 + \delta_2 + \delta_3 = \sqrt{3/2} = \text{height}. \qquad (25)$$

For the distances δ'_i to the circumscribed triangle, corresponding to the distances D_i, one obtains

$$\delta'_i = (1 - f_i)\sqrt{3/2} = (r_{jk}/r)\sqrt{6}. \qquad (26)$$

Also of interest are the lines along which any one of the angles of the molecule is constant. If one angle is fixed, say ϕ_3, then ϕ_2 is given by ϕ_1 because the sum of all three is π. A parametric representation of the curves $\{\xi_1(\phi_1), \xi_2(\phi_1)\}$ for constant ϕ_3 is then obtained by substituting the expression of Eq. (9) or Eq. (11), with $\phi_3 = \text{constant}$ and $\phi_2 = \pi - \phi_3 - \phi_1$, in the equations

$$\begin{aligned} \xi_1 &= (f_2 - f_1)/\sqrt{2} \\ \xi_2 &= (2f_3 - f_1 - f_2)/\sqrt{6} \qquad (27) \end{aligned}$$

which follow from Eq. (18). Figure 6 displays the curvilinear grid of the curves

$$\phi_j = 15°, 30°, 45°, 60°, 75°, 90°, 105°, 120°, 135°, 150°, 180°$$

for $j = 1, 2, 3$. The plot shows that all acute molecules lie inside the shaded area enclosed by the lines $\phi_1 = 90°$, $\phi_2 = 90°$ and $\phi_3 = 90°$ which become tangent at the corners where two nuclei coincide. The three unshaded areas correspond to the three types of obtuse molecules.

4.2 Illustrative examples

Since the first octant diagonal of the (s_1, s_2, s_3) space penetrates the shape coordinate triangle at the origin $\xi_1 = \xi_2 = 0$, this point corresponds to the equilateral molecule with sides $s/3$. From what has been said earlier, it is also apparent that the isosceles molecules correspond to points on the lines from the three corners, through the origin to the mid-points of the opposite sides. For example, the ξ_2 axis contains the isosceles molecules with the nucleus N_3 at the apex. From the

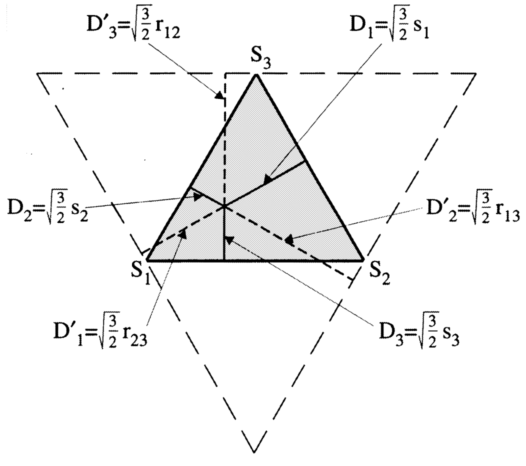


Fig. 5. Definition of D_1, D_2, D_3 for Eq. (21) and D'_1, D'_2, D'_3, for Eq. (23)

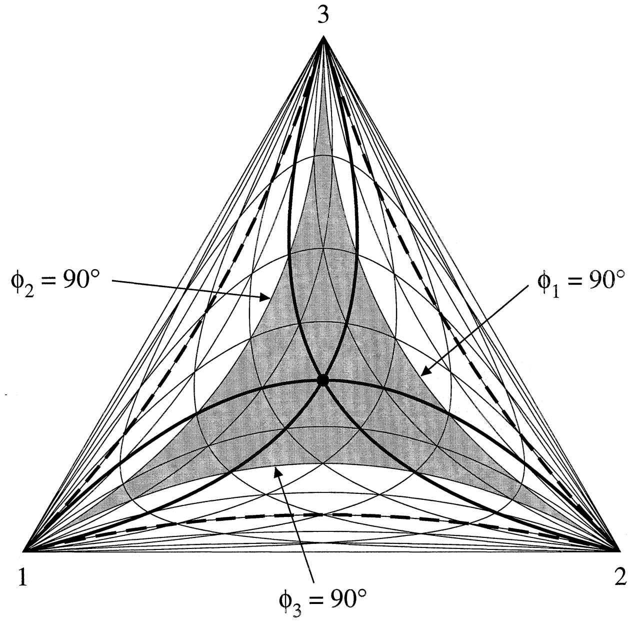


Fig. 6. Curves of constant angle in scale-independent shape coordinate space. The curves $\phi_j =$ constant are convex towards corner j. Increments: $\Delta\phi_j = 15°$. Bold: 60°. Dashed: 120°. Shaded area: ϕ_1, ϕ_2, ϕ_3 all $\leq 90°$

discussion of the three-dimensional parameter space, it is also seen that the three sides of the shape-coordinate triangle correspond to linear molecules, the points on the side connecting the corners i and j representing the linear molecules with the nucleus N_k lying between the nuclei N_i and N_j.

Some illustrative examples of oblique triangles are displayed in Fig. 7.

Of importance is the case of linear molecules. If nucleus N_3 lies between nuclei N_1 and N_2, then one has

$$\begin{aligned} &\phi_1 = 0, \quad \phi_2 = 0, \quad \phi_3 = \pi, \quad r_{12} = r_{13} + r_{23}, \\ &s_3 = 0, \quad s_1 = r_{13}, \quad s_2 = r_{23}, \quad s = s_1 + s_2, \end{aligned} \tag{28}$$

and the shape factors become

$$\begin{aligned} &f_1 = s_1/(s_1 + s_2) = r_{13}/(r_{12} + r_{23}), \\ &f_2 = s_2/(s_1 + s_2) = r_{23}/(r_{12} + r_{23}), \\ &f_3 = 0 \end{aligned} \tag{29}$$

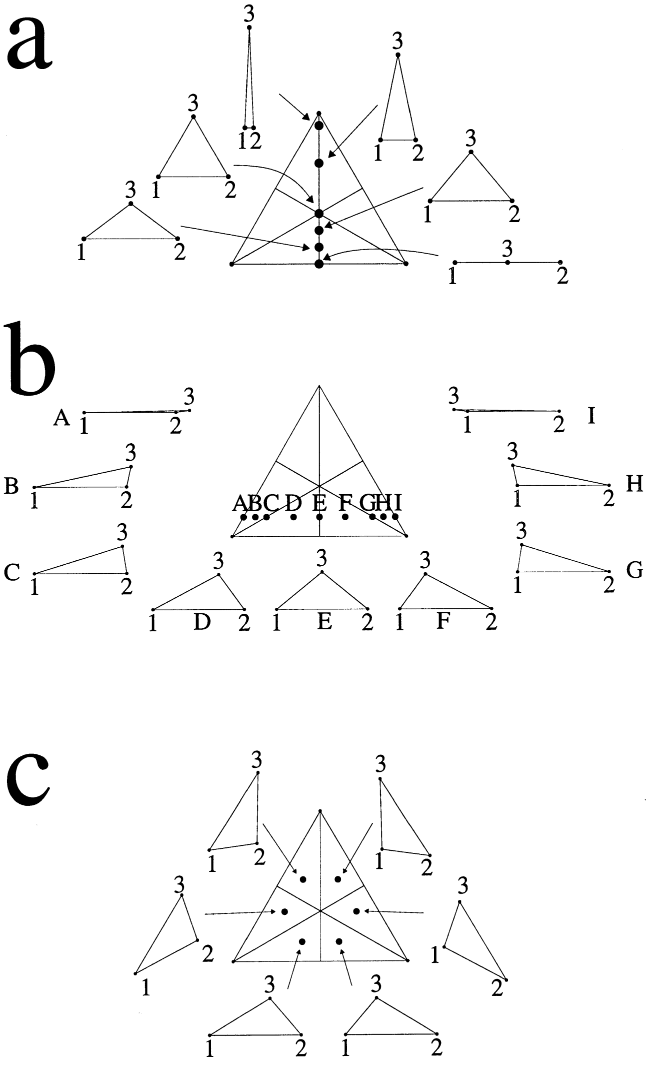


Fig. 7a-c. Examples of molecular shapes for selected points in the scale-independent shape coordinate plane. **a** Isosceles molecules with N_3 at the apex. **b** Molecules with constant r_{12} distance. **c** Molecules related to each other by permutations of atoms

By virtue of Eqs. (24) and (29), we have $\delta_3 = 0$ so that the parameter point lies indeed on the (1–2) side of the shape-coordinate triangle. Such a point is shown in Fig. 8. Since the corner angle is 60°, one obtains for the segments σ_1, σ_2 on the triangle side [note Eq. (24)]

$$\begin{aligned} \sigma_1 &= \delta_2 2/\sqrt{3} = f_2\sqrt{2} = \sqrt{2}r_{23}/(r_{13} + r_{23}), \\ \sigma_2 &= \delta_1 2/\sqrt{3} = f_1\sqrt{2} = \sqrt{2}r_{13}/(r_{13} + r_{23}), \end{aligned} \tag{30}$$

which indeed add up to the side length $\sqrt{2}$. The coordinates of this point are therefore found to be

$$\xi_1 = \sigma_1 - \sqrt{2}/2 = \sqrt{2}(r_{23} - r_{13})/r, \quad \xi_2 = -1/\sqrt{6}. \tag{31}$$

4.3 Symmetry

The C_s symmetry, possessed by all triatomic molecules, is intrinsic to the entire perimetric parameter space. The latter is invariant with respect to the molecular C_s group.

If the nuclei N_1 and N_2 are identical, then all points on the plane spanned by the x_3 and $x_2 = s\xi_2$ axes correspond to molecules with C_{2v} symmetry, i.e. the plane $x_1 = 0$ is "C_{2v} restricted". Moreover, any two points in the remainder of the coordinate space obtained from each other by reflection through this plane describe two molecules which are each other's mirror image with respect to a plane bisecting the N_1—N_2 bond. Consequently, any molecular function which is invariant with respect to the interchange of N_1 and N_2 will have C_s symmetry *in the* (x_1, x_2, x_3) *coordinate space*, with $x_1 = 0$ defining the C_s mirror plane.

If all three atoms are identical, then analogous considerations show that not only the plane of $x_1 = 0$, but also the two planes obtained from it by rotation through ± 120° around the x_3 axis are (1) C_{2v} restricted and (2) symmetry planes for any function that is invariant under the permutation of *any* of the nuclei. In fact, any such function possesses C_{3v} symmetry in the coordinate space. The x_3 axis corresponds to molecules with D_{3h} symmetry.

In the subspace defined by $x_1 = 0$ which, when N_1 and N_2 are identical nuclei, corresponds to C_{2v} symmetry, i.e. isosceles molecules, it is often convenient to make use of the coordinates x and y defined in Fig. 9. It is therefore useful to know the coordinate grid defined by the lines s = constant and x_2 = constant in the (x, y) plane.

From the definitions of s and x_2 [see Eqs. (3)–(5),(15)] and from Fig. 9, one readily derives

$$s = s(x, y) = (x^2 + y^2)^{1/2} + x, \tag{32}$$

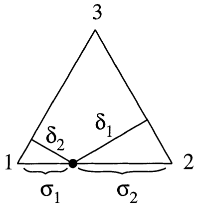


Fig. 8. Coordinate point of a linear molecule $N_1N_2N_3$

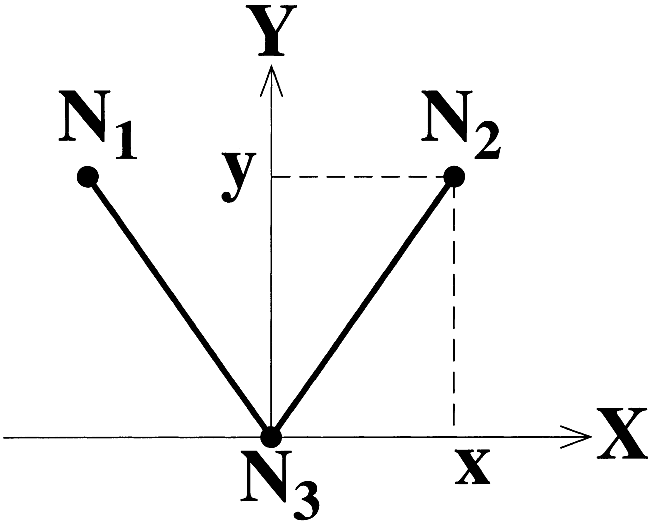


Fig. 9. Coordinates x and y for isosceles molecules

$$x_2 = x_2(x,y) = [(x^2+y^2)^{1/2} - 2x]\sqrt{2/3}. \tag{33}$$

The inversion of these equations yields

$$x = x(s,x_2) = s/3 - x_2/\sqrt{6}, \tag{34}$$

$$y = y(s,x_2) = s[(1+\sqrt{6}x_2/s)/3]^{1/2}. \tag{35}$$

From Eqs. (32) to (35), one readily finds the lines of constant s and x_2. The lines $s = \text{constant}$ are given by the parabolas

$$y^2 + 2sx = s^2, \quad (s = \text{const}). \tag{36}$$

The lines $x_2 = \text{constant}$ are given by the hyperbola branches

$$6(x + x_2\sqrt{2/3})^2 - 2y^2 = x_2^2, \quad (x_2 = \text{const.}) \tag{37}$$

$$x \geq \max\left\{0, -x_2\sqrt{3/8}\right\} \tag{38}$$

The sections of these curves in the first quadrant are displayed in Fig. 10a. The points on the two axes correspond to the limits of x_2 for given s. The points on the x axis correspond to the lower limits $x_2 = -s/\sqrt{6}$; the points on the y axis correspond to the upper limits $x_2 = 2s/\sqrt{6}$. This is illustrated in Fig. 10b, which also indicates the values of x and y at these limits.

The lines corresponding to the shape coordinates $\xi_2 = x_2/s = \text{constant}$ are obtained by dividing Eq. (34) into Eq. (35), which yields the straight lines

$$\left[3\left(1+\sqrt{6}\xi_2\right)\right]^{1/2} x - \left(1 - \frac{1}{2}\sqrt{6}\xi_2\right) y = 0, \quad (\xi_2 = \text{const.}) \tag{39}$$

These are displayed in Fig. 10c.

5 Extended shape coordinate space

Certain continuous deformations of the molecule are not accounted for by continuous coordinate changes in the discussed coordinate space, namely the in-plane inversions of a triatomic molecule through the linear structures. If, in the spirit of considering only internal coordinate variations, out-of-plane motions are excluded, then these inversions change a clockwise ordering of the three atoms into a counterclockwise ordering. Such deformations can be accounted for by suitably enlarging the coordinate space, as illustrated in Fig. 11. The consecutive deformations exhibited in Fig. 11a are represented by the sequence of points in the coordinate space of Fig. 11b, where a second coordinate triangle has been attached to the original one through reflection with

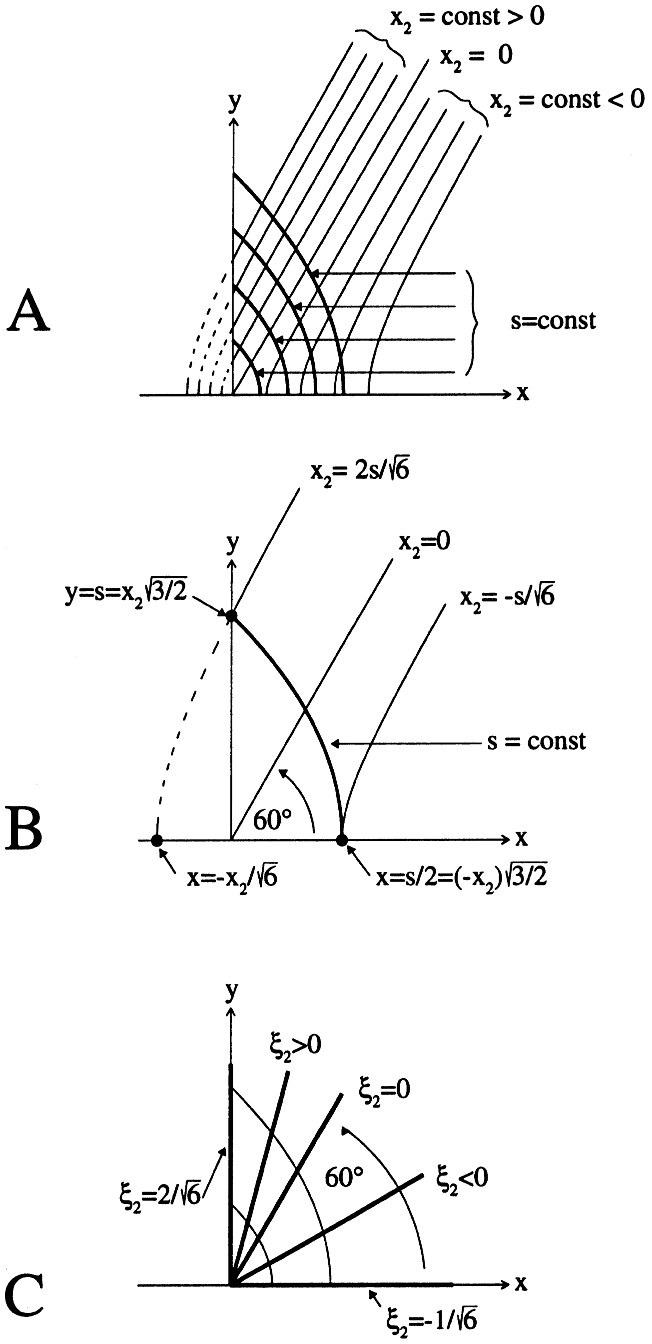
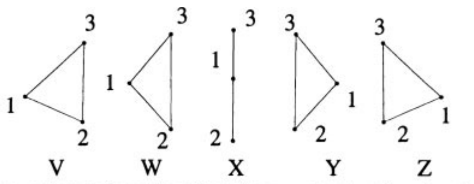
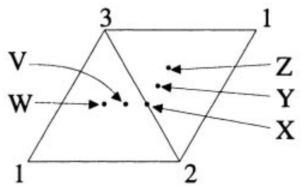


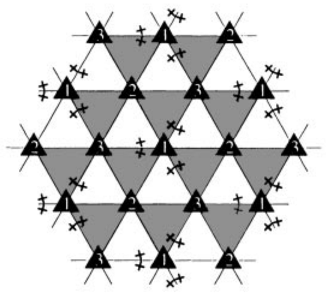
Fig. 10a-c. Lines $s = \text{constant}, x_2 = \text{constant}$, and $\xi_2 = \text{constant}$ on the (x,y) plane



A. In-plane molecule inversions keeping r_{12}=const. and $r_{12}+r_{23}+r_{13}$ = const.



B. Extended shape coordinates for deformations of A.



C. Complete extended shape coordinate space. 1,2,3: Triangle corners. Shaded: Clockwise order. White: Anticlockwise order of atoms. ▲: Trigonal axes. Solid lines: mirror planes. Crosses: Equivalent coordinate points.

Fig. 11. Complete extended shape coordinate space

respect to the line connecting corners 2 and 3. Further thought shows that this kind of enlargement has to be repeated in all directions over the entire $x_1 - x_2$ plane in order to cover all possible molecular in-plane inversions by continuous coordinate curves. The entire $x_1 - x_2$ plane is thus divided into coordinate triangles, half of them with clockwise ordering, the other half with counterclockwise ordering of atoms, as shown in Fig. 11c. They are related by the translational grid of symmetry elements also shown in that figure: a set of trigonal rotation axes and three sets of reflection axes. Such translational symmetry grids are typical for internal shape coordinates. (Another such translational grid for another set of internal coordinates has been discussed in an investigation of another PES [10].)

The enlargement of the coordinate triangle serves the purpose of visualizing the energy changes for all nuclear rearrangements. As an example, Fig. 12 displays the PES contours of the ground state of ozone [1] in the enlarged parameter space. (Ozone has, of course, an additional C_{3v} symmetry within each triangle, as discussed in Sect. 4.3.) The white areas near the triangle corners are the areas where two atoms come so close that the energy becomes extremely high and is not calculated. This would not be the case, of course, if the purely electronic PES were plotted (i.e. without nuclear repulsions). Manifestly, only energy values within the dashed line of Fig. 12 are required for understanding all in-plane inversions through linear configurations.

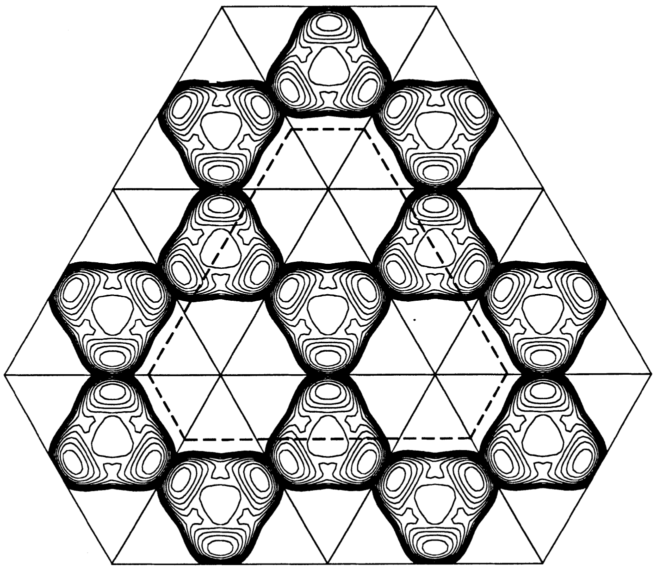


Fig. 12. Extended potential energy surface of ozone ground state for $s = 2.4$ Å

The described coordinate space extension has one severe shortcoming. Namely, the PES contours have discontinuous first derivatives on the edges separating the different coordinate triangles, a fact which is also illustrated by Fig. 12. This will present problems if critical points of interest have linear geometries.

It may also be noted that, for very small values of s, all three atoms come very close to each other, so that the PES tends to infinity and becomes highly repulsive. These regions of coordinate space are thus inaccessible and there is no need to deal with very small and negative values of the coordinate x_3.

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