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Symmetry and periodicity of potential surfaces: a test for multicenter interactions*

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Symmetry and periodicity of potential energy surfaces of chemical reactions and conformational changes are determined by the symmetry properties of the nuclear frameworks of all possible nuclear configurations of the given overall stoichiometry. For example, a mirror plane of a nuclear configuration implies a mirror plane of the potential surface (or that of the potential energy hypersurface in higher dimensions), and a local rotational symmetry of substituents implies a translational symmetry, that is, periodicity of the potential surface, if the latter is defined in terms of the usual bond length/bond angle internal coordinates. Such symmetry relations on potential surfaces are rather trivial consequences of molecular symmetry properties; however, when taken *collectively* for entire domains of nuclear configurations, they lead to nontrivial conclusions. Whereas symmetry properties and energy contents of individual conformations can be studied locally within limited domains of the potential surface, a *global analysis* of the potential surface may reveal significantly more. In this note, some consequences of the above approach are explored, and a simple test is proposed for the detection and evaluation of the importance of *multicenter interactions* in conformers related to one another by bond rotations.

Key words: Potential surfaces — Conformation analysis — Reaction topology — Multicenter interactions — Symmetry — Periodicity

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

Introduction

Any global interpretation of a potential energy hypersurface model involves an entire family of molecules and conformers, characterized by a common overall stoichiometry and some constraint on the electronic state [1-7]. Most frequently, this latter constraint is formulated within the adiabatic approximation [8, 9], and one may formally consider all possible molecules and conformations involving a fixed set of N nuclei of specified nuclear charges and k electrons in some specified formal electronic state. Such a global representation is rather complex for all but the simplest of chemical systems, if for no other reason, simply as a consequence of the high dimension, $3N$-6, of the potential energy hypersurface associated with the N nuclei. That dimension rapidly becomes uncomfortably high if N is greater than four or five.

It is natural to search for simplifying features on such multidimensional hypersurfaces, and one of the most obvious tools that may be exploited is the symmetry of the potential energy hypersurface. This ($3N$-6)-dimensional symmetry is determined by the three-dimensional, laboratory-frame symmetry properties of all the possible nuclear configurations composed from the N nuclei. The connection between symmetries in the two spaces (the three-dimensional euclidean space of the laboratory frame, and the ($3N$-6)-dimensional nuclear configuration space, ${}^{3N\text{-}6}R$, above which the potential energy hypersurface is defined) is rather trivial and is often exploited in the simplest case of conformational problems involving bond rotations. For example, if the ($3N$-6)-dimensional nuclear configuration space ${}^{3N\text{-}6}R$ is defined in terms of the usual bond length/bond angle internal coordinates, then a two-dimensional mirror plane of a laboratory-frame nuclear configuration implies a ($3N$-7)-dimensional mirror plane of the nuclear configuration space ${}^{3N\text{-}6}R$, and a ($3N$-6)-dimensional mirror plane of the potential energy hypersurface. Similarly, a local rotational symmetry of substituents in the laboratory frame implies a ($3N$-6)-dimensional translational symmetry within the nuclear configuration space ${}^{3N\text{-}6}R$, that is, periodicity of the potential energy hypersurface. Furthermore, if within the local internal coordinate system of the nuclear configuration space ${}^{3N\text{-}6}R$ the point assigned to the united atom configuration is unique (a condition not necessarily fulfilled by an arbitrary set of internal coordinates), then the three-dimensional symmetry element of a point of inversion within the laboratory frame implies a ($3N$-6)-dimensional symmetry element of a point of inversion within the corresponding domain of the nuclear configuration space ${}^{3N\text{-}6}R$. Note that, in contrast to the symmetry elements mentioned above, this does *not* imply that a point of inversion should also exist on the potential energy hypersurface itself, since the hypersurface is embedded in a ($3N$-5)-dimensional space, where the additional dimension is energy, and a laboratory-frame point of inversion does not in general imply an inversion along the ($3N$-5)th (energy) coordinate. A similar restriction applies for rotation-inversion symmetry elements S_n.

Note that laboratory-frame mirror planes and points of inversion are formally "inherited" in a rather straightforward manner by the nuclear configuration space

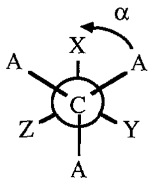
${}^{3N\text{-}6}R$, by assigning a higher-dimensional symmetry element of the same type to each. However, local *rotational* symmetry in the laboratory frame corresponds to a fundamentally different type of symmetry of space ${}^{3N\text{-}6}R$: to *translational* symmetry.

Whereas symmetry properties of *individual* configurations are of great utility in the analysis of their physical and chemical properties, the study of the symmetry properties of an entire potential energy hypersurface can reveal the *symmetry relations among various chemical processes, chemical reactions and conformational changes.* These collective properties represent qualitatively more than information on the symmetry properties of a sequence of individual configurations, since global properties represent global constraints. Various global approaches to chemical problems are finding applications in theoretical chemistry: in reaction kinetics [10, 11], in potential surface analysis [12–14], and in the study of more general chemical functionals [15]; a detailed bibliography can be found in [7].

In this note we shall suggest an application of a global approach to the problem of three-center, and in general, multicenter interactions along conformational reaction paths. We shall show that the relative importance of such multicenter interactions can be tested by analyzing the degree of asymmetry of the potential energy hypersurface, within the above global approach. Whereas there is no unique definition for a quantitative measure of the degree of asymmetry (the degree of *deviation* from a given symmetry) of individual nuclear configurations, one such measure can be given for the potential energy hypersurface, in terms of an integral of an energy-like quantity. In the definition of this measure we shall exploit the only truly peculiar symmetry relation between the laboratory-frame euclidean space and space ${}^{3N\text{-}6}R$: the correspondence between laboratory-frame rotation and ${}^{3N\text{-}6}R$ space translation, mentioned above.

The interrelation between periodicity and reflection symmetry along conformational potential surfaces

We shall use an example in order to introduce some of the intuitive concepts required for the proposed test of multicenter interactions. Consider the conformational problem of the substituted ethane derivative A_3C–CXYZ, where we assume that different letters stand for different monatomic substituents. In particular, we shall investigate the two-dimensional potential energy surface defined in terms of two internal coordinates: the C–C bond rotation coordinate, α, and the C–C bond stretching coordinate, r, illustrated in Fig. 1. For the sake of simplicity we shall assume that the A_3C moiety has a local C_3 symmetry element, with an axis coincident with the C–C bond axis, which is preserved for all conformational motions confined to the plane defined by the internal coordinates α and r. That is, we shall consider an ideal conformational problem involving rotation and stretching along only one, single formal C–C bond: the combinations of rigid rotations of the A_3C group, and simple stretching of the C–C bond, interconnecting two rigid molecular fragments. The forthcoming analysis is the simplest if we assume that A,X,Y, and Z are all simple, monatomic substituents.



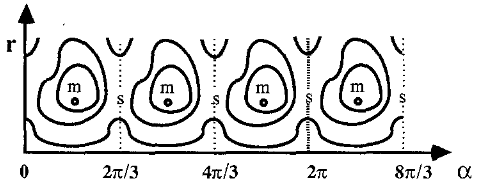


Fig. 1. Periodic potential surface of the conformational problem of C–C bond rotation (α) and C–C bond stretching (r) of substituted ethane derivative A_3C-CXYZ. Due to multicenter interactions the potential surface has no mirror lines. Letters *m* and *s* stand for minima and saddle points, respectively

Evidently, for any fixed bond length r all conformations with a substituent A and substituent X eclipsed are equivalent, hence the potential energy surface is periodic in coordinate α by a period of $2\pi/3$. Consider three conformations for a given r value: the eclipsed conformation (r, α_0), where

$$\alpha_0 = 2\pi, \tag{1}$$

and two additional conformations, (r, α'), and (r, α''), derived from the eclipsed conformation (r, α_0) by taking

$$\alpha' = \alpha_0 - \Delta\alpha, \tag{2}$$

and

$$\alpha'' = \alpha_0 + \Delta\alpha, \tag{3}$$

respectively, where $\Delta\alpha$ is a positive angle less than $2\pi/3$, otherwise arbitrary,

$$0 < \Delta\alpha < 2\pi/3. \tag{4}$$

In the two conformations (r, α') and (r, α'') precisely the same nucleus-nucleus distances are present; however, these pair distances are distributed among the nuclei in a different way. For example, consider the nucleus A that is eclipsed with nucleus X in configuration (r, α_0). In configuration (r, α') this nucleus A is at distances d_{AX}, d_{AY}, and d_{AZ} from nuclei X, Y, and Z, respectively, as illustrated in Fig. 2. In configuration (r, α'') the same nucleus A has the same distance d_{AX} from nucleus *X*. By contrast, precisely the same d_{AY} and d_{AZ} distances will not in general belong to the same nucleus *A* in the new configuration (r, α''). Instead, distance d_{AY} will belong to one and d_{AZ} will belong to the other of the remaining two nuclei of type A. In the new configuration (r, α'') all the old pair distances are accounted for. However, in general no nucleus A will have all its pair distances the same as in conformation (r, α'). In particular, note that the two conformations (r, α') and (r, α'') are not in general the mirror images of each other.

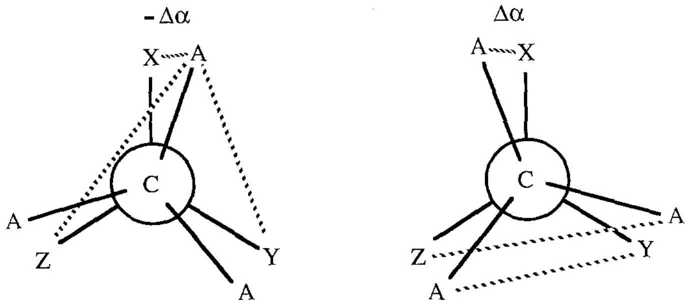


Fig. 2. Although the two rotamers depicted in this figure contain precisely the same set of pair interactions, these pair interactions are redistributed among different pairs (only the redistribution of the pair interactions AX, AY, and AZ of one of the A atoms of the first rotamer is shown by *dotted lines*). This redistribution leads to differences in the multicenter interactions in the two rotamers, which are responsible for the lack of reflection symmetry along lines of constant α of the potential surface shown in Fig. 1.

The above observation implies an important general result. Evidently, the electron distribution is controlled by the location of the nuclei. Consequently, if the conformational energy could be represented as a sum of two-center interactions, then the preservation of pair distances would lead to the same energy value for the two conformations (r, α') and (r, α''):

$$E^{\#}(r, \alpha') = E^{\#}(r, \alpha''). \tag{5}$$

The above case (indicated by #) is henceforth referred to as the case of additive pairwise interactions (API). The line characterized by

$$\alpha = \alpha_0 = 2\pi, \tag{6}$$

and all the lines with angles

$$\alpha = \alpha_0 + k2\pi/3, \qquad k = 0, \pm 1, \pm 2, \pm 3, \ldots. \tag{7}$$

correspond to *lines of reflection* of the API *potential energy* surface. Stating this in different terms, in the above API case the potential energy surface exhibits

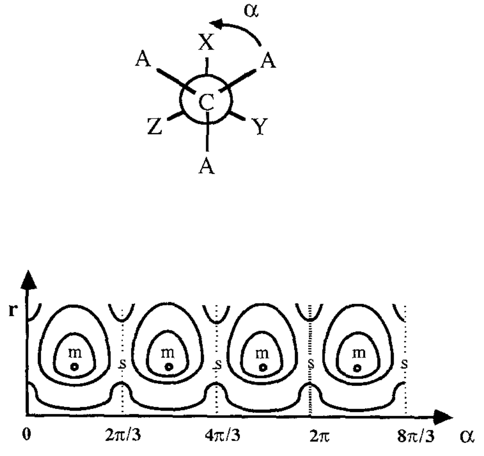


Fig. 3. The ideal additive pairwise interaction potential surface of the conformational problem of Fig. 1. Note that, in addition to periodicity, this potential surface also has reflection lines at the $\alpha = k(2\pi/3)$, $k = 0, \pm 1, \pm 2, \ldots$ values

additional symmetries. An example for the API case, analogous to that of Fig. 1, is shown in Fig. 3.
In real conformational problems the above assumption that molecular conformational energy can be represented as a sum of two-body interactions does not hold in general. Even if precisely the same d_{AX} distance is found for a given nucleus A in the two conformations (r, α') and (r, α''), the fact that the remaining interactions of A are different in the two conformers implies that the actual AX interactions will also be different, in spite of the common internuclear distance d_{AX}. This may be interpreted as a many-body effect: a change in the AX interaction, caused by changes in other interactions involving the same nucleus A.

This many-body effect implies that for the true conformational energy $E(r, \alpha)$ Eq. (5) is not necessarily valid, that is,

$$E(r, \alpha') \neq E(r, \alpha'') \tag{8}$$

is possible. Consequently, lines characterized by angle coordinates $\alpha = \alpha_0 + k2\pi/3$, $k = 0, \pm1, \pm2, \pm3, \ldots$ are not necessarily lines of reflection of the true potential energy surface $E(r, \alpha)$ and the additional symmetry present for the simpler model is missing.

It is important to note, however, that the two-body interactions are usually dominant, and actual potential surfaces of the above type often show strong resemblance to the API case, where reflection symmetry is present in addition to periodicity.

An energy integral as a measure of "missing symmetry" and test for multicenter interactions

It is possible to define a quantitative measure of the deviation from the API case of reflection symmetry. Consider the following function:

$$f(r, \alpha) = E(r, \alpha) - E(r, -\alpha). \tag{9}$$

For the function $E^{\#}(r, \alpha)$ the angle $\alpha = \alpha_0 = 2\pi$ and the angle $\alpha = 0$ correspond to lines of reflection. Consequently, the function $f(r, \alpha)$ is the difference of surface $E(r, \alpha)$ and its reflected image $E(r, -\alpha)$, the latter obtained by reflecting $E(r, \alpha)$ along one of the lines of reflection $(\alpha = 0)$ of the API surface $E^{\#}(r, \alpha)$. If E is replaced by $E^{\#}$ in Eq. (9), then $f(r, \alpha)$ is identically zero:

$$f(r, \alpha) = 0. \tag{10}$$

However, for true conformational surfaces of the above type the function $f(r, \alpha)$ is not in general zero and at some point (r, α) its actual value

$$f(r, \alpha) \tag{11}$$

may serve as a *local* measure for the "degree of deviation" from reflection symmetry.

Alternatively, one may ask the question, how large is in general the deviation from reflection symmetry along the entire potential surface in a *global* sense. For any property of the surface it is sufficient to carry out a test or analysis over the *unit cell* of a periodic potential. In our conformational problem the unit cell is the product of the two representative intervals for variables r and α:

$$[0, \infty)\otimes[0, 2\pi/3]. \tag{12}$$

One may take the following integral of function $f(r, \alpha)$ over the unit cell,

$$g = \int_0^\infty \int_0^{2\pi/3} |f(r, \alpha)|\, dr\, d\alpha, \tag{13}$$

as a *global* measure of deviation from reflection symmetry along the potential energy surface. For an API potential energy surface $E^{\#}$, involving no multicenter interactions, the above global measure g is zero,

$$g = 0, \tag{14}$$

as is evident from Eq. (10). For real potential surfaces of variables r and α, the above integral g may also serve as a *global* measure of the importance of multicenter interactions.

The above function f and integral g can be generalized for periodic potential energy hypersurfaces of dimension n (e.g. $n = 3N\text{-}6$), where n is higher than two. Let us assume that angle α is an internal coordinate along which the hypersurface $E(\boldsymbol{r}, \alpha)$ is periodic, and the (n-1)-dimensional vector $\boldsymbol{r}$ represents collectively all the remaining internal coordinates. Then, by analogy with the two-dimensional case, Eq. (9), a function $f(\boldsymbol{r}, \alpha)$ can be defined as

$$f(\boldsymbol{r}, \alpha) = E(\boldsymbol{r}, \alpha) - E(\boldsymbol{r}, -\alpha). \tag{15}$$

At point $(\boldsymbol{r}, \alpha)$ of the n-dimensional nuclear configuration space ${}^nR$ the above function $f(\boldsymbol{r}, \alpha)$ is a local measure of the deviation from reflection symmetry along planes (in general, hyperplanes) of the space ${}^nR$. These planes or hyperplanes are characterized by a constant α value, at which an API energy hypersurface $E^{\#}(\boldsymbol{r}, \alpha)$ of the same type of internal coordinates $(\boldsymbol{r}, \alpha)$ has mirror planes, or in general, (n-1)-dimensional mirror-hyperplanes. Evidently, Eq. (10) also holds for higher dimensional API hypersurfaces so for $E(\boldsymbol{r}, \alpha) = E^{\#}(\boldsymbol{r}, \alpha)$

$$f(\boldsymbol{r}, \alpha) = 0. \tag{16}$$

Consequently, function $f(\boldsymbol{r}, \alpha)$ is also a *local* measure of the deviation of the actual hypersurface $E(\boldsymbol{r}, \alpha)$ from the analogous API hypersurface involving only additive, pairwise interactions. That is, function $f(\boldsymbol{r}, \alpha)$ is a *local* test of the contribution of multicenter interactions.

Note that the internal coordinate α along which a potential energy hypersurface $E(\boldsymbol{r}, \alpha)$ is periodic is not necessarily unique. Reflections by two hyperplanes characterized by the constancy of two different periodic internal coordinates, α and α', correspond to two different physical conditions and to two different sets of conformational motions. In addition, they test two different sets of multicenter interactions.

By arguments analogous to those of the two-dimensional case, one may define a *global* measure for the degree of loss of reflection symmetry along the entire potential energy hypersurface. If the distinguished angle variable α is periodic by δ, and if the $(n-1)$-dimensional formal unit cell of the remaining internal coordinates is denoted by ${}^{n-1}U$, then the actual n-dimensional unit cell ${}^{n}U$ of the hypersurface may be regarded as the product set

$$ {}^{n}U = {}^{n-1}U \otimes [0, \delta]. \tag{17}$$

For the n-dimensional case the global measure g is defined as

$$ g = \int_{{}^{n-1}U} \int_{0}^{\delta} |f(\boldsymbol{r}, \alpha)| \, d\boldsymbol{r} \, d\alpha. \tag{18}$$

The above integral g is zero for API potential energy hypersurfaces. However, g is not in general zero for actual potential energy hypersurfaces involving all interactions and it provides a *global test* for the contribution of multicenter interactions.

Applications of this test of multicenter interactions, within the frameworks of various approximations to the molecular wavefunction, will be reported in a forthcoming publication.

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