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## **Ambiguity of Symmetry**

Istvan Hargittai\*<sup>[a]</sup>

**Abstract**: Beyond the universality of the symmetry concept, there are different emphases on its application in different branches of science. Chemistry, being between particle physics and astrophysics, represents a bridge in, and a utilitarian approach to, the application of the symmetry concept, which has proved immensely fruitful in twentieth-century science. Some pivotal discoveries, especially in structural chemistry, molecular biology, and materials science, emerged by relaxing some of the stipulations of the classical teachings about symmetry. This highly personal presentation relies on ideas expressed by a number of notable individuals in recent science, among them J. Desmond Bernal, Francis Crick, Ronald J. Gillespie, Aleksandr I. Kitaigorodskii, Alan L. Mackay, George A. Olah, Linus Pauling, Roger Penrose, Dan Shechtman, James D. Watson, Steven Weinberg, and Eugene P. Wigner.

Keywords: Ambiguity · chirality · history of science · scientific discovery · symmetry

#### 1. Introduction

Five years ago, I published another essay in the *Israel Journal of Chemistry, Dan Shechtman's Quasicrystal Discovery in Perspective*, and I concluded my presentation by mentioning my encounter with Eugene P. Wigner (Figure 1).<sup>[1]</sup> That I am starting the present essay with mentioning Wigner, signifies a pleasant continuity.

Wigner's contributions were fundamental to the understanding of the importance of the symmetry concept for science. In his terminology, symmetries and invariances were interchangeable. According to Wigner, the invariances make it possible to formulate the laws of nature. He underlines that "the first and perhaps the most important theorem of invariance in physics" is that "absolute time and position are never essential initial conditions."<sup>[2]</sup> In everyday language, this means that the validity of the physical laws of nature are independent of the location where and the point in time when we are considering them.

Wigner formulated the consecutiveness of invariances, laws of nature, and the events we observe and experience; that is, the physical phenomena:

The concept of initial conditions has utmost importance, even for dividing the sciences into disciplines in a meaningful way. Wigner says: "Other sciences which deal with what we physicists consider to be initial conditions, are, among others, geography and descriptive astronomy."<sup>[3]</sup> These examples explain what initial conditions mean. Events described by geography and descriptive astronomy depend on the place and time – initial conditions – hence, they are not governed by the laws of nature.

True laws of nature do not depend on the initial conditions. Sciences such as geography and descriptive astronomy "tell us only facts." Physics and mathematics are concerned with regularities. These are the two extremes. There are then sciences that are in between the two extremes, such as, for example, botany, zoology, and the medical sciences - according to Wigner. By geography, he means descriptive geography. As we move from descriptive geography toward physical geography, likewise, from descriptive geology to physical geology, and so on, we move from sciences solely concerned with initial conditions toward sciences concerned with regularities, that is, the laws of nature. "Physics does not endeavor to explain nature. In fact, the great success of physics is due to a restriction of its objectives: it only endeavors to explain the regularities in the behavior of objects. ... The regularities in the phenomena which physical science endeavors to uncover are called the laws of nature."<sup>[4]</sup> This formulation reflects Wigner's modesty, and his modesty may have helped him to recognize this profound limitation of the natural sciences.

Before Wigner (Figure 2), physicists used to use symmetry considerations for solving particular issues, whereas Wigner applied them in a most general way. One of the most profound messages Wigner conveyed to me was about the universality of the symmetry concept; that its validity cuts across the disciplines. We need to keep this in mind in the discussion following here, because there will be peculiarities assigned here to various disciplines

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**Figure 1.** Eugene P. Wigner with the author in 1969 at the University of Texas at Austin.

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modeling of molecular structures. He is the Editor-in-Chief of the international Springer journal Structural Chemistry. His recent books include Wisdom of the Martians (with B. Hargittai), Budapest Scientific (with M. Hargittai), Great Minds (with B. Hargittai and M. Hargittai), Buried Glory, Drive and Curiosity, Judging Edward Teller, Martians of Science, The Road to Stockholm, and Symmetry through the Eyes of a Chemist (with M. Hargittai). His most recent edited books are, both with Balazs Hargittai, Culture of Chemistry and Science of Crystal Structures.



Figure 2. Eugene P. Wigner in the late 1960s (courtesy of the late Martha Wigner Upton).

for an easier understanding and more efficient utilization of the symmetry principle.

Broken symmetry may be as important as symmetry itself. Such broken symmetries appear, for example, under the conditions above certain temperatures, and this has special significance for chemistry. As Steven Weinberg (Figure 3) explains:<sup>[5]</sup>

"The laws that govern atoms are completely symmetrical with respect to direction. There's nothing in nature that says that one direction in the laboratory, whether it's east and west or up and down, is any different from any other direction. On the other hand, when atoms join to form a molecule, for example, when three oxygen atoms join to form an ozone molecule, that's a triangle that points in a definite direction. It breaks the rotational invariance of the laws of chemical attraction by forming a particular object that has not the full rotational symmetry but a smaller symmetry, just rotations by multiples of sixty degrees. If you had a more complicated molecule, there'd be no symmetry left, yet the underlying laws are perfectly symmetrical. Those molecules only exist below a certain temperature. You



Figure 3. Steven Weinberg in 1998 at the physics department, University of Texas at Austin (photograph by I. Hargittai).

can always restore the symmetry by heating them sufficiently so the molecules break up into a gas. If you have a gas of monoatomic oxygen, without worrying about the walls, it is symmetrical; all directions are the same."

When the monoatomic gas has a distribution equivalent in all directions, perfect disorder emerges; thus, we equate this perfect disorder with symmetry. Further, according to Weinberg:<sup>[6]</sup>

"Perfect disorder is symmetry. To have order, for example in a crystal, you break the symmetry. You only have symmetry by finite rotations. A crystal of salt is invariant when you change your point of view by rotation of 90 degrees around various axes. It's a cubic crystal. But if you have molten sodium chloride, then there's no preferred direction at all. You've created complete disorder, as far as the directions are concerned. People in condensed matter physics very often use the terms order and disorder rather than broken symmetry and restored symmetry although they are very closely related.

"The symmetries that we talk about in elementary particle physics are not broken because of any particular object has formed. The physical state that breaks the symmetry is not a molecule or a crystal. It is empty space. The vacuum, although it's perfectly symmetrical with regard to rotations in space, or translations in space, is not invariant with respect to changes in your point of view about which particles are viewed. It's the vacuum that distinguishes the neutrino from the electron, or the weak interactions from the electromagnetic interactions. The reason that the photon is massless whereas the other particles on the same symmetry multiplet, the W and the Z particles, are very heavy, is because of the way they propagate through the vacuum."

At this point, I have to refer to my long conversation with Yuval Ne'eman in 2000 in Stockholm. In the course of that conversation, he told me that on the basis of symmetry considerations, he had predicted the mass of the Higgs particle, which at that time had not yet been observed. Ne'eman said, "If and when the Higgs [particle] will be found and its mass measured, I would now like to advertise my theory and people to know that I had predicted it."<sup>[7]</sup> As Ne'eman died before the actual observation of the Higgs particle, I find it important to mention his prediction here.

Weinberg stressed the importance of the symmetry of the laws of nature, but the symmetry of objects is also important, and in chemistry, and in molecular biology, they play a distinct role:<sup>[6]</sup>

"It is important that the sugars in living things are right-handed and the amino acids are left-handed, but it's not the most fundamental about them. On the other hand, the symmetries of nature are the deepest things we know about nature. It's much easier to learn about the symmetries of a set of laws than about the laws themselves. For example, long before there was any clear understanding of the nuclear forces, it was clear that there was a symmetry that the nuclear forces obeyed that related neutrons and protons and it said that they behaved the same way with regard to the strong forces."

We shall mention the issue of chirality later in our discussion. At this point, we once again bring up the relationship of crystals and symmetry to illustrate how different interpretations may there be depending on the kind of question we are asking about them. In chemistry, when crystallization occurs, there is translational symmetry on the inside, in addition to other symmetries, let alone the symmetry of the external shape. On a deeper level, as we speak about the external shape of a crystal, it already points to the breaking of translational symmetry, because translational symmetry does not include an ending of such symmetry; it should extend to infinity. In reality, although the crystal is finite, it is usually large enough to consider it infinite (from the point of view of a diffraction experiment, for example).

If we take the point of view in physics, there is a different approach, and this is what Weinberg emphasizes: "When you have a crystal, condensed from a liquid, the crystal breaks translational invariance. The crystal is in one location and if you translate the crystal by an infinitesimal amount, you have a different crystal, the atoms are clearly moved, the crystal has a definite location, it's here, not there. That means that translational invariance is a broken symmetry."<sup>[8]</sup>

In the examples that follow, mostly chemical structures will figure, and a utilitarian approach to symmetry. Emphasis will be on the application of the symmetry concept in a variety of discoveries in chemistry. The limits of the applicability or the utility of this concept will be indicated at places. We will mention examples in the complementarity in crystal structures; structure elucidation of large, biologically important molecules; determination and prediction of the molecular geometries and structural variations of simple molecules, among them, the intriguing carbocations; the discovery of fullerenes and quasicrystals; and chirality.

#### 2. Complementarity in Crystal Structures

For our discussion, the main interest of complementarity in crystal structures is in that the most symmetrical arrangements are by far not the most frequent among crystal structures. By now, with hundreds of thousands of crystal structures available in databases, the preeminence of complementarity is a well-established fact. The Soviet-



Figure 4. Aleksandr I. Kitaigorodskii lecturing (courtesy of Irena Akhrem).

Russian crystallographer, Aleksandr I. Kitaigorodskii (Figure 4),<sup>[9]</sup> predicted the relative frequencies of symmetry occurrences of all the 230 kinds of symmetry in crystal structures. He made his predictions long before hundreds of thousands of structures had become available. His initial goal was even more ambitious: it was finding regularities in how molecules build up crystals, and on such a basis predicting crystal structures as soon as the composition of a new substance would become available. This goal has so far proved elusive.

In the late 1930s, the German physicist Pascual Jordan suggested that interactions between identical or nearly identical parts of molecules represent the advantageous mode of building up stable systems (Zur Frage einer spezifischen Anziehung zwischen Genmolekülen; To the question of a specific attraction between gene-molecules).<sup>[10]</sup> In contrast, Linus Pauling and the physicistturned-biologist Max Delbrück argued for precedence for interactions between complementary parts, rather than identical ones.<sup>[11]</sup> The title of their short communication was The Nature of the Intermolecular Forces Operative in Biological Processes. It is unlikely, especially under the war-time conditions, that Kitaigorodskii (Figure 5) could have been familiar with the Pauling-Delbrück paper. Yet Kitaigorodskii, independently, declared a research program, "The close packing of molecules in crystals of organic compounds" in the then still-existing English-language Soviet physics journal.<sup>[12]</sup> The program was based on his views on the preeminence of attractive interactions between complementary molecular shapes. He predicted that "the mutual location of molecules is determined by the requirements of the most close-packing."

Kitaigorodskii used his own so-called structure-finder, a simple stand to which he fastened wooden models of molecules of the same arbitrary shape and examined the densest packing of virtually all 230 symmetry variations.



Figure 5. "Complementary Kitaigorodskii" (drawing by and courtesy of lstván Orosz).

He found that the highest frequency occurrence of molecular packing should be that characterized by two-fold rotational symmetry (Figure 6). This is what corresponds to the complementary arrangement of molecules in which



**Figure 6.** Densest packing with space groups (top) p1 and (bottom) p2. After Ref. [15].

protrusions of one molecule meet with cavities of the other molecule. This is spatial complementarity. Molecular packing characterized with symmetry planes is not impossible, but it is rather disadvantageous for densest packing (Figure 7). In other words, "lower symmetry packs better."<sup>[13]</sup> Today's wealth of data on hundreds of thousands of crystal structures has proved Kitaigorodskii's predictions, demonstrating the correctness of his far-sighted vision of the interactions directing crystal architecture.<sup>[14]</sup>

#### 3. Alpha-helix and Double-helix Structures

During the first half of the twentieth century, the existence of biological macromolecules was not yet generally accepted, but the efforts to establish the nature of biolog-

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**Figure 7.** The presence of symmetry planes in the space groups (top) pm and (bottom) pmm hinder densest packing. After Ref. [15].

ical substances and to uncover their structures were going on. Michael Polanyi and Herman F. Mark subjected fibrous materials to X-ray diffraction in the 1920s, at the Kaiser Wilhelm Institute in Berlin. The experiments on cellulose indicated the presence of crystallites in cellulose that were oriented in the direction of the fiber axis. Furthermore, Polanyi and Mark observed characteristic changes when they stretched the cellulose fibers. X-ray crystallography was becoming the preeminent tool for the structure determination of biopolymers.

Linus Pauling (Figure 8) joined early the quest for uncovering the structure of biopolymers. He had been the foremost structural chemist accumulating information about the structure and bonding of small molecules, including amino acids, the building blocks of proteins. Hemoglobin was the first protein that attracted Pauling's interest. As is well known, hemoglobin carries the oxygen in our organism. There was also a British group in Cambridge working on the structure of hemoglobin that had



Figure 8. Linus Pauling's autographed photograph (courtesy of the late Linus Pauling).

chosen this protein for their inquiry, independent of Pauling's interest.

There were two types of proteins known; for example, hair, horn, porcupine quill, and fingernail belonged to one, and silk to the other. Hair in its normal state and in its wet state showed differences in their X-ray diffraction patterns, according to the experiments by William T. Astbury. He called one alpha keratin, and the other beta keratin. The beta keratin was the stretched form and the Xray pattern of the beta keratin state of hair was similar to the X-ray pattern of silk. Pauling decided to start his studies with alpha keratin. He launched a complex investigation in which he used all his accumulated knowledge of the structure of small molecules and all his knowledge about the correlation of geometrical features and bonding peculiarities of molecular structure. Understanding chemical bonding was as important as collecting X-ray diffraction data. Thus, knowing about the double-bond character of the peptide bond meant a drastic reduction of possible protein structures, because the bond configuration about such a bond had to be planar or nearly planar. This piece of information helped Pauling to drastically reduce the number of possible models. Nonetheless, at the time this was during the second half of the 1930s - Pauling still did not have enough information about the details of the protein structures to be able to propose a model that would be in agreement with all the X-ray diffraction evidence he possessed. Among the unknown factors, it was not known how the diversity among the building blocks that is, among the amino acid units of the proteins would influence the overall structure of the protein molecule.

About a decade later, Pauling continued his quest for the protein structures. At this time - this was in 1948 - he decided to ignore the fact that the building block amino acids were different from each other, and assumed them to be equivalent. This was a huge simplification; in a way, it was the introduction of translational symmetry in the protein chain, where, rigorously considering it, it did not exist. His subsequent results justified this simplification. Once he could consider the protein chain more uniform than it was, he could apply to it a mathematical theorem according to which an asymmetric object can be converted into an equivalent asymmetric object by the application of rotation-translation. Subsequent and repeated application of this operation - and this is also prescribed by the mathematical theorem - produces a helix. This was a breakthrough and one of the factors that permitted Pauling to reach it was his bravely overlooking the absence of rigorous symmetries among the building blocks of the protein chain.

Pauling realized the fruitfulness of building models. He prepared a rudimentary drawing of the protein chain (Figure 9) – using uniform amino acids – and determined the possible models emerging from folding the drawing in such a way that satisfied the possibility of hydrogen-bond



**Figure 9.** Linus Pauling's sketch of the polypeptide chain in 1948. Pauling folded the paper along the creases and arrived at the alpha helix (courtesy of the late Dorothy Munro, Linus Pauling's long-time personal assistant).<sup>[16]</sup>

formation that he had also found to be present in the desired structure.<sup>[16]</sup> The result showed one problem that did not seem to be surmountable, viz., the turn about the chain did not correspond to an integer number of amino acids. This, again, lowered the degree of symmetry of the emerging structure. In a bold move, Pauling decided to ignore this deficiency of his model, as there really was no stipulation that such a symmetry requirement should be fulfilled. Once he went ahead, two models appeared satisfactory, of which one could be discarded readily and the other was the model he called alpha helix. The Cambridge (UK) group that was working on the protein structures simultaneously with Pauling came up with numerous models, none of which turned out to be acceptable. Pauling's competitors did not apply the simplifications that Pauling did with such success.

There was at least one general lesson from Pauling's achievement in producing the alpha-helix structure of proteins: "Pauling's approach to solving this complex problem was exemplary in focusing on what was essential and ignoring what had little consequence. When it turned out that the turn about the chain did not correspond to an integer number of amino acids, hinting at less than perfect symmetry, he did not let himself bothered by this. He thus expanded the realm of crystallography toward structures that were not part of classical crystallography yet included literally vital substances."<sup>[17]</sup>

Francis Crick (Figure 10) and James D. Watson (Figure 11) published their suggestion for the structure of deoxyribose nucleic acid (DNA) in April 1953 (Figure 12). They wrote that their "structure has two helical chains each coiled round the same axis. ... The two chains (but not their bases) are related by a *dyad* [two-fold axis] *perpendicular to the fibre axis.* Both chains follow right-handed helices, but owing to the dyad the sequences of the atoms in the two chains run in opposite directions"<sup>[18]</sup> (emphasis by me). It may be argued that the



Figure 10. Francis Crick in 2004 in La Jolla (photograph by I. Hargittai).



Figure 11. James D. Watson in 2000 in the author's home in Budapest (photograph by I. Hargittai).

mention of dyad here is equivalent to a two-fold axis of rotation ( $C_2$  symmetry), but one wonders why Watson and Crick were not more explicit about this feature of the structure. There was some ambiguity about how Watson and Crick, each of them separately, handled the presence of symmetry in the DNA structure.<sup>[19]</sup> The impression has formed "that for Watson, the  $C_2$  symmetry of the structure was not as revealing as it was for Crick. Back in 1951, he [Watson] wrote to Delbrück, 'Our method is to completely ignore the X-ray evidence.<sup>[20]</sup> In February 2004, Crick noted that Watson did not understand the significance of  $C_2$  symmetry of the DNA structure.<sup>[21]</sup>

In his book, *What Mad Pursuit*, Crick was more selfcritical with respect of the difficulties in recognizing the importance of  $C_2$  symmetry and its implication for the DNA structure. He notes that discovering base-pairing was more the result of serendipity than logical thinking. It would have been more elegant to come to the right conclusion by logical thinking: "first to assume Chargaff's

**Figure 12.** Artist's rendition of the double helix of DNA; Bror Marklund's sculpture in front of the Biomedical Center of Uppsala University (photograph by I. Hargittai in 1997).<sup>[a]</sup>

rules were correct and thus consider only the pairs suggested by these rules, and second, to look for the dyadic symmetry suggested by the C2 space group shown by the fiber patterns."<sup>[22]</sup>

At this point, it is of interest to mention that Watson's apparent indifference to the  $C_2$  symmetry of the DNA structure was not characteristic of his general demeanor towards symmetry. When the work on the DNA structure was temporarily halted in Cambridge, and he joined the investigation of tobacco mosaic virus, he did consider its symmetry. Donald Caspar described the story:<sup>[23]</sup>

"It was Jim Watson who recognized the helical symmetry in tobacco mosaic virus (TMV). This had grown out of the work on the DNA structure. [W. L.] Bragg was the director of the Cambridge laboratory where Watson and Crick were working on DNA, and he [Bragg] found out in 1952 that DNA research was also going on in Randall's lab at King's College in London. Bragg called Crick and Watson into his office and ordered a moratorium on the DNA work in his lab. At that time it was considered ungentlemanly in Great Britain to work on the same problem as your colleagues and to compete with them. That's when Watson switched temporarily to the TMV problem. He recognized that TMV was a helix and applied to it the theory of diffraction by helical structures that Crick had worked out. The helical symmetry that Watson had

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inferred had turned out to be incorrect and Rosalind Franklin had got it right a few years later. But in 1952, DNA was more exciting than TMV, and when Bragg learned about the ongoing work on DNA by Linus Pauling in Pasadena, he lifted the moratorium and gave Watson and Crick full support to resume their DNA work."

The structure of TMV did have helical symmetry, though different from the initial suggestion. It has a rod shape and the proteins envelop, with a helical array, a single-stranded RNA molecule (Figure 13). At first sight, biological macromolecules and other polymeric structures appear very similar. There is, though, an important difference. To build a model for a biological macromolecule, the starting point should correspond to a nucleation event. According to Aaron Klug (Figure 14), "The key to biological specificity is a set of weak interactions. A polymer chemist could start building the model in the



Figure 13. The model of TMV (courtesy of Aaron Klug).



**Figure 14.** Aaron Klug with the TMV model in 2000 at the laboratory of Molecular Biology in Cambridge (photograph by I. Hargittai).

<sup>[</sup>a] The area surrounding the sculpture has been built in since the time the snapshot was taken.

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middle or at any other point." In contrast, for building the models of biological macromolecules, it is "important to find the special sequence for initiating nucleation."<sup>[24]</sup> Incidentally, preparing a model of TMV was a task for the world exhibition in Brussels in 1958. Rosalind Franklin was a major contributor to elucidating the TMV structure. By the time her group was preparing for the Brussels exhibition, she was already gravely ill and died in the same year as the world exhibition took place.

The terms helix and spiral are rigorously distinguishable, but everyday language often, and even scientists sometimes, use them interchangeably. Helical symmetry is when a constant amount of translation is accompanied by a constant amount of rotation. For spiral symmetry, both the amounts of translation and accompanying rotation change gradually and regularly (Figure 15). The biological molecules have helical, rather than spiral, symmetry, whereas oscillating reactions, accompanied by color changes, may form beautiful spiral patterns (Figure 16).<sup>[25]</sup>

The two-fold rotational symmetry of the DNA doublehelix structure is in beautiful correlation with the function of this biological macromolecule. Symmetry does not appear in such a directly visible way for many other bio-



**Figure 15.** Artist's rendition of a true double spiral, detail of "The Inner Light" by Gidon Graetz, in the garden of the Weizmann Institute in Rehovot (photograph by I. Hargittai).



Figure 16. Enhancing spiral pattern in a reacting Belousov-Zhabotinsky system (drawing by and courtesy of the late Endre Kőrös).



**Figure 17.** The structure of the photosynthetic reaction center with approximate  $C_2$  symmetry (courtesy of Johann Deisenhofer).

logical systems. Sometimes it does, but the function is still not correlated in any perceivable way with it. An example is the attractive two-fold symmetry of the photosynthesis reaction center, yet what, if anything, it means for the process of photosynthesis remains a puzzle (Figure 17). Johann Deisenhofer described the moment of the discovery as follows:<sup>[26]</sup>

"It was extremely exciting to localize these features and build models for them. When I stepped back to see the arrangement, the unexpected observation about it was symmetric. There was symmetry in the arrangement of the chlorophyll that nobody had anticipated. Nobody, to this day, completely understands the purpose of this symmetry. I think it can be understood only on the basis of evolution. I think that the photosynthetic reaction started out as a totally symmetric molecule. Then it turned out to be preferable to disturb its symmetry, sticking to an approximate symmetry but changing subtly the two halves of the molecule. Because of the difference in properties of the two halves, the conclusion had been, before the structure came out, that there cannot be symmetry; that it has to be an asymmetric molecule. Now, when people looked at the structure, it looked totally symmetric to the naked eye. That realization was the high point I will never forget."

#### 4. Structural Complications for Simple Molecules

Ronald J. Gillespie's (Figure 18) valence shell electron pair repulsion (VSEPR) model or theory predicts the geometry of the molecule on the basis of the number of electron domains (bonding pairs, lone pairs, multiple bonds) in the valence shell of its central atom.<sup>[27]</sup> The predicted shapes and symmetries depend not only on the general number of electron domains, but to various ex-

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Figure 18. Ronald J. Gillespie in 1998 in Austin, Texas (photograph by I. Hargittai).

tents, also on the nature of those domains, whether they are single bonds, lone pairs, or multiple bonds.

In all VSEPR considerations, spherical symmetry of the valence shell of the central atom is assumed, and that all electron domains are at equal distances from the nucleus of the central atom (Figure 19). The geometries may be determined as the ones assigned to the minimum of the potential energy. Its terms can be expressed as  $V_{ij} = k/r_{ij}^{n}$ , where k is a constant,  $r_{ij}$  is the distance between the points *i* and *j* in the spherical valence shell, and the exponent *n* is large for strong and small for weak repulsions. The value of *n* is generally much larger than what it would be for merely electrostatic interactions, but it is not known. The great advantage of the model is that it



Figure 19. A variety of VSEPR geometries.

Early on, the determination of the structure of xenon hexafluoride was a conspicuous success for the model. As soon as the substance was produced, some rudimentary molecular calculations predicted that the molecule has the highly symmetrical  $(O_h)$  regular octahedral shape. However, according to the VSEPR model, XeF<sub>6</sub> should be described as an  $AB_6E$  system, where A is the central atom, the ligands B are linked to it by an electron pair each, and there is also a lone pair of electrons, E, in the valence shell of xenon. Hence, the molecule cannot have a regular octahedral shape. When Gillespie predicted a distorted geometry for  $XeF_6$ , the subsequent experimental studies suggested C<sub>3v</sub> symmetry, or even C<sub>2v</sub> symmetry, for the molecule could be derived from the O<sub>h</sub> structure by small distortions. Further work, however, vielded less unambiguous results. The suggestion was that it all depended on the stereochemical activity of the lone pair of electrons. In the case of a stereochemically active lone pair, the molecule is expected to display fluxional behavior, i.e., rapidly interconverting series of configurations. In the case of stereochemical nonactivity, a rather rigid structure should be present. The case of XeF<sub>6</sub>, which was such a convincing case for the utility of the VSEPR model, has become an example of its limitations.<sup>[28]</sup>

Rigorously applying the VSEPR arguments in cases where they should work impeccably, it is interesting to note that it is not always the highest symmetries that emerge in molecular structures. Thus, the seemingly analogous molecules OPF<sub>3</sub> and OClF<sub>3</sub> should be described in VSEPR formulation as CAB<sub>3</sub> and C(E)AB<sub>3</sub>, respectively, where A is the central atom, C and B are ligands, and E is a lone pair of electrons in the valence shell of the chlorine atom. The bond configuration of OPF<sub>3</sub> has a distorted tetrahedral shape of  $C_{3v}$  symmetry, whereas OClF<sub>3</sub> has a trigonal bipyramidal arrangement of the five electron domains and a bond configuration of C<sub>s</sub> symmetry (Figure 20). The electron domains, whether they represent a single bonding pair, a multiple bond, or a lone pair, have different spatial requirements, and accordingly, repulsion strengths, in the valence shell. They are, in decreasing order: lone pair, multiple bond, and single bond.



**Figure 20.** OPF<sub>3</sub> is of  $C_{3v}$  symmetry and OCIF<sub>3</sub> is of  $C_s$  symmetry.

Further refinement of the model is necessary when, for example, single bonds connect ligands of different electronegativities. An example is the comparison of the molecular symmetries of  $F_3PCl_2$  and  $F_2PCl_3$  (Figure 21). Both



**Figure 21.** In both trigonal bipyramidal structures of  $PF_3Cl_2$  and  $PF_2Cl_3$ , the fluorine atoms occupy axial positions and the chlorine atoms occupy equatorial positions.  $PF_3Cl_2$  is of  $C_{2\nu}$  and  $PF_2Cl_3$  is of  $D_{3h}$  symmetry.

structures have  $C_3AB_2/C_2AB_3$  descriptions, and accordingly, trigonal bipyramidal bond configurations. However, the bonds leading to more electronegative ligands (fluorine) have smaller space requirements in the valence shell of the central atom than the bonds leading to less electronegative ligands (chlorine). Further, in the trigonal bipyramidal configuration, not all positions are equivalent in their space requirements. The surroundings of the axial positions are more crowded than those of the equatorial positions. Hence, the bonds to fluorine are expected to be in axial positions, and the bonds to chlorine in equatorial positions. The corresponding symmetries are, indeed,  $C_{2v}$ for  $F_3PCl_2$ , and  $D_{3h}$  for  $F_2PCl_3$ .

In the examples mentioned above, we focused on the variations of molecular symmetry. Changing the nature of the ligands may also cause characteristic changes in the bond lengths and bond angles in a series of substituted derivatives without changes in the molecular symmetry. Sometimes, it is fruitful to look at the variations in the distances between atoms not connected by chemical bonding, especially when the ligand atoms are large with respect to the central atom. Generally speaking, the VSEPR rules may work best for small ligands relative to the central atom. The relative weight of the nonbonded interactions in shaping the geometry of the molecule increases with increasing ligand size with respect to the central atom.

Thus, for example, retaining the constancy of such nonbonded distances may be looked at as the primary factor in the realization of certain structures. Here, we single out the remarkable constancy of the O...O nonbonded distances of the sulfone groups in a series of substituted sulfone molecules,  $O_2SXY$  (Figure 22). The O...O distance hardly changes from being 2.48 Å in a series of free sulfone molecules, while the lengths of the S=O bonds vary up to 0.05 Å, and the O=S=O bond angles vary up to 5 degrees, depending on the nature of the X and Y ligands.<sup>[29]</sup> The variations in the sulfone series could be visualized by a tetrahedron of the two oxygen atoms and



Figure 22. Tetrahedral sulfur configurations. From the left: sulfones; sulfuric acid; and alkali sulfates.

the X and Y ligands about the central sulfur atom, with the two oxygen atoms firmly taking the positions of two of the vertices of the tetrahedron. Depending on the nature of the X and Y ligands, the central sulfur atom would be sliding along the bisector of the OSO angle, changing the SO bond lengths and OSO bond angles, but keeping the O...O distances unchanged. The recognition of the constancy of the O...O distances in an extended series of sulfone molecules enhanced the possibilities of the combined application of electron diffraction and microwave spectroscopy in the accurate determination of related molecular structures.

Even systems as simple as metal dihalides may have complications in their molecular symmetry. The free molecules of dihalides of alkaline earth metals used to be considered linear, of  $D_{\infty h}$  symmetry. We have learned, however, that this holds only for the dihalides of lighter metals, viz., beryllium and magnesium. Toward the dihalides of heavier metals, especially when combined with smaller halogens, the molecules are bent, as of C<sub>2v</sub> symmetry. There are a few structures in between that are called quasilinear. They are characterized with a small energy barrier on the bending potential energy distribution at the position of the linear configuration, but this energy barrier may even be below the ground-state energy level. A broad and flat minimum of the bending potential energy curve is typical for quasilinear molecules. They are floppy and very little energy input suffices to bend or straighten such molecules (Figure 23).

The symmetry descriptions  $D_{\infty h}$  and  $C_{2v}$ , as well as quasilinearity, refer to the minimum positions on the bending potential-energy curve. There is a related, but rigorously distinguishable, case when a molecule that is strictly linear in the minimum energy position appears nonetheless as bent from certain experimental structure elucidations. This happens most conspicuously when the bending vibrations of a metal dihalide appear as low-frequency, large-amplitude motion. Any experimental technique that determines the time-averaged structure and for which the interaction time is longer than the bending motion of the molecule, will yield a bent geometry, even when the molecule is linear in the minimum energy position. In terms of the halogen-halogen nonbonded distance, in the linear configuration, this will be exactly twice the bond length; in any bent position of the molecule, the halogen-halogen



**Figure 23.** Bending motions and a sampler of potential energy functions. Top: bending vibrations of a linear triatomic molecule, where *r* is the instantaneous distance between the end atoms and  $r_e$  is the equilibrium distance of the linear configuration ( $r < r^e$ ). Bottom: Comparison of bending potential functions for linear and bent models of symmetric triatomic molecules.

distance will be shorter than twice the bond length. However, this is only an apparent deviation from linearity. Such a difference between molecular shapes and symmetries of the minimum position structure (called also equilibrium structure) and the average structure is characteristic not only of the triatomic  $AB_2$  molecules, but any polyatomic molecule. Again, the higher the probability of low-frequency, large-amplitude deformation motion, the larger the difference expected between the equilibrium and average structures.

Generally speaking, fluxional molecular behavior decreases the probability of unambiguous determination and description of molecular shape and symmetry. Permutational isomerism is an example of fluxional behavior. R. Stephen Berry discovered it for trigonal bipyramidal structures, and it is called Berry pseudorotation (Figure 24).<sup>[30]</sup> Permutational isomerism is when different structures with different symmetries of the same molecule interconvert. Identical atoms permute among nonequivalent sites in these processes. The VSEPR model suggests only a slight energy preference for the trigonal bipyramidal model (D<sub>3h</sub>) over the square pyramidal one (C<sub>4v</sub>) and they easily interconvert.

Above, we have already considered, in passing, the important relationship of the interaction time required by the physical phenomena on which the experimental technique is based, and the lifetime of the structure being measured. The interaction times are relatively long for



**Figure 24.** Berry-pseudorotation of PF5-type molecules, with a potential energy function; and R. Stephen Berry in 2001 in Erice, Italy (photograph by I. Hargittai).

the techniques of NMR spectroscopy, and very short for the diffraction techniques. Vibrational spectroscopy is somewhere in between. Thus, for example, for the rapidly interconverting  $AB_5$  trigonal bipyramidal geometries, NMR spectroscopy may yield information only about the average A–B bond, whereas electron diffraction may distinguish the axial and the equatorial A–B bonds.

Berry-pseudorotation introduces a great deal of ambiguity into the description of structures analogous to PF<sub>5</sub>. It plays an important role in the chemistry of large, biologically important molecules, as well as in the physicalphilosophical considerations of the concept of molecular structure. Frank Westheimer found far-reaching implications of Berry-pseudorotation when he and his students investigated the hydrolysis of phosphate ester. In this process, the four-coordinate phosphorus becomes five-coordinate as it goes into its transition state, then becomes fivecoordinate through pseudorotation, and then returns to four-coordinate. The driving force of this process is in the difference in bond strengths. In the five-coordinate situation, the bonds are weaker in the axial positions than in the equatorial positions. The formation of a weaker axial bond precedes its rearrangement into a stronger equatorial bond, while another equatorial bond becomes a weaker axial bond and breaks off. This is a pivotal event for important biochemical processes.[31]

The philosophical implication of Berry-pseudorotation may be formulated in this way: it appears to be a paradox that in the process of pseudorotation, identical nuclei occupy observably nonequivalent sites. Quantum mechanics prescribes that identical particles, electrons, for example, but not only electrons, have to be indistinguishable,

and the wavefunction for identical particles reflects this indistinguishability. In contrast, in chemistry, we operate with the distinguishability of different sites in molecules. The considerations of the time scales, interaction time versus the lifetime of a structure, resolve this apparent paradox.

Above, we have considered the appearance of a bent average geometry for a linear molecule, as a result of averaging over all configurations during bending vibrations. We have also mentioned that the interaction time in NMR spectroscopy may be too long to distinguish between axial and equatorial bonds in trigonal bipyramidal systems. It is possible, however, to conduct a series of NMR experiments with a changing relationship of the two time scales, demonstrating, for example, the coalescence of NMR lines, which in a fast experiment correspond to different chemical shifts, and in a slow experiment correspond to the average.<sup>[32]</sup>

Symmetry-lowering may happen due to the Jahn–Teller effect. A nonlinear, symmetrical nuclear configuration in a degenerate electronic state is unstable and gets distorted – this is how it removes the electronic degeneracy until it achieves a nondegenerate state, according to the formulation of the Jahn–Teller effect.<sup>[33]</sup> A typical case of Jahn–Teller distortion is the structure of crystalline manganese trifluoride. The six fluoride ions surround the manganese ion in six-coordination in its structure. In a regular octahedral arrangement, the six manganese-fluoride distances would be uniform, but this is not the case. Rather than having  $O_h$  symmetry, there is the lower  $D_{4h}$  symmetry with two different manganese-fluorine distances.

Recently, the Jahn–Teller effect of a free molecule in gaseous manganese trifluoride was demonstrated with reliable geometrical parameters.<sup>[34]</sup> For this molecule, the highest possible symmetry would be  $D_{3h}$ , but the Jahn–Teller effect lowers it to  $C_{2v}$  symmetry. Rather than having three 120 degree bond angles, there are two of 106 and one of 148 degrees; also, one of the Mn–F bonds is shorter than the other two. The distortion stabilizes the molecule. These are not apparent, but real geometrical changes that are present in the minimum position of the potential energy distribution and characterize the corresponding equilibrium structure.

The complexity of the  $CH_5^+$  structure rivals that of the XeF<sub>6</sub> molecule. This carbocation has had special significance in organic chemistry, as its discovery was related to the beginning of a whole new direction in the discipline.<sup>[35]</sup> This new direction has transformed hydrocarbon chemistry from a rather inert kind of domain into the source of exceptional wealth of new substances. It became possible by the application of superacids that stabilized the otherwise short-lived carbocations and enabled the otherwise unreactive covalent carbon-carbon and carbon-hydrogen bonds to become reactive. The discoverer, George A. Olah (Figure 25), could rightly con-



**Figure 25.** George A. Olah in 1995 at the Budapest University of Technology and Economics (photograph by I. Hargittai).

clude: "The realization of the electron donor ability of shared electron pairs could one day rank equal in importance with G. N. Lewis' realization of the electron donor unshared pairs."<sup>[36]</sup>

The carbocation  $CH_5^+$  contains a five-coordinated carbon – note, however, that it is not a hypervalent carbon, only hypercoordinated. Thus, it could be viewed as containing five electron domains such that each is somewhat poorer in electrons than a two-electron covalent bond. In that case, the five-coordination and five-electron domain carbocation could have a trigonal bipyramidal arrangement of  $D_{3h}$  symmetry, according to the predictions of the VSEPR model. This turned out to be not the case.

Early quantum chemical computations predicted a C<sub>s</sub> symmetry structure for CH<sub>5</sub><sup>+</sup>, which would correspond in Olah's description to the presence of three two-electron two-center bonds and one two-electron three-center bond.<sup>[37]</sup> This may be a structure of either having a high degree of localization, or having a fluxional character by exchanging the positions of the two-electron two-center bonds and the two-electron three-center bond. Provided that the C<sub>s</sub> symmetry structure is in a sufficiently deep energy minimum, it could be observable in experiments if the lifetime of this structure is long enough, as compared with the interaction time of the experimental technique employed. There had been attempts to apply the concept of pseudorotation to the highly fluxional CH<sub>5</sub><sup>+</sup>, however, if the CH<sub>3</sub><sup>+</sup> plus H<sub>2</sub> description holds, pseudorotation would not be the right approach to its description.

Recent high-resolution spectroscopic experiments on  $CH_5^+$  have suggested the presence of structures corresponding to Olah's description (Figure 26).<sup>[38]</sup> We have to keep in mind, however, that all the spectroscopic evidence are also consistent with a highly fluxional character of  $CH_5^+$ : "the five proton swarm around the central



Figure 26. Two-electron two-center bonds and two-electron threecenter bonds in protonated alkanes.<sup>[40]</sup>

carbon".<sup>[39]</sup> Olah's model of three two-electron covalent bonds and one two-electron three-center bond may thus be only one of the models that can be singled out from among a multitude of models. They, in their totality as an average, may be considered as a more realistic representation of this carbocation that Oka called the "enfant terrible" of structural chemistry.<sup>[39]</sup>

Although the VSEPR model could not predict unambiguously the geometry of  $CH_5^+$ , some analogous structures appear consistent with VSEPR predictions. The geometry of mono-positively charged carbocation  $\{[(C_6H_5)_3PAu]_5C\}^+$  containing five-coordinate carbon is trigonal bipyramidal (Figure 27). According to Olah, this



Figure 27. The trigonal bipyramidal mono-positively charged carbocation  $\{[(C_6H_5)_3PAu]_5C\}^+$  and the octahedral di-positively charged carbocation  $\{[(C_6H_5)_3PAu]_6C]^{2+}.^{[40]}$ 

gold complex is an isolobal analog of  $\text{CH}_5^+$ , hence the isolobal analogy would suggest a trigonal bipyramidal geometry for  $\text{CH}_5^+$ , which is not the case (see above). A similar discussion could apply to the  $\text{CH}_6^{2+}$  carbocation and the {[(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PAu]<sub>6</sub>C]<sup>2+</sup> carbocation. Six equivalent electron domains would favor a regular octahedral geometry of O<sub>h</sub> symmetry and the six bonding directions point to the vertices of a regular octahedron in the gold complex. In contrast, the computations have suggested the presence of two two-electron covalent bonds and two two-electron three-center bonds for the CH<sub>6</sub><sup>2+</sup> carbocation. There is then the CH<sub>7</sub><sup>3+</sup> carbocation, for which one two-electron covalent bond and three two-electron threecenter bonds would apply by analogy.

#### 5. Five-fold Symmetry in Extended Structures

Five-fold symmetry is just as common in the world of molecules as any other symmetry. This is not the case, however, in extended structures. Five-fold symmetry was an excluded symmetry in classical crystallography. Two important discoveries in the 1980s, both in materials science – one in the world of molecules and the other in extended structures – were related to five-fold symmetry. Each of the two discoveries was eventually awarded a chemistry Nobel Prize.

The discovery of buckminsterfullerene (first of its existence,<sup>[41]</sup> then, its production<sup>[42]</sup>) made waves due to the beauty of its structure and the fact that it was a heretofore unknown modification of carbon. The  $C_{60}$  molecule is of truncated icosahedral shape. There is a presence of fullerene-type structures and their fragments in nanotubes. Considering today's importance of nanoscience and nanotechnology, even a symbolic impact by the buckminsterfullerene discovery in this development is noteworthy.

The icosahedral arrangement of atoms has interested researchers because they considered it as containing some of the clues of the puzzle of the progression from isolated molecules to extended systems. The icosahedral arrangement caught J. Desmond Bernal's (Figure 28) eye early on. He was interested in the structure of liquid water and the icosahedral arrangement was viewed as the one preventing the crystallization of water. Linus Pauling also showed distinct interest in icosahedral structures.



Figure 28. J. Desmond Bernal giving a speech (photograph by and courtesy of Alan L. Mackay).

Alan L. Mackay (Figure 29) enveloped a sphere with an icosahedral shell consisting of 12 spheres and enveloped this structure by another shell, and the second shell was arranged over the first so that the spheres were in contact along five-fold axes. When he added a third shell, the structure already contained 147 spheres, and this is what has been known as the Mackay icosahedron or Mackay polyhedron.<sup>[43]</sup> When icosahedra are packed together, like in the Mackay polyhedron, they gradually curve up to form a closed system. In addition to the Mackay polyhedron, another example is the icosahedral polyoma virus (Figure 30).<sup>[44]</sup>



**Figure 29.** Alan L. Mackay in 1982 in Budapest (photograph by I. Hargittai).



Figure 30. Icosahedral polyoma virus drawn after Adolph et al.[44]

In a parallel development, Roger Penrose (Figure 31) invented a two-dimensional pattern of hierarchic tessellation of the plane, which was regular, that is, it was constructed by well-defined rules, but it was not periodic.<sup>[45]</sup>



**Figure 31.** Roger Penrose in 2000 in Oxford, UK (photograph by I. Hargittai).

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Penrose had seen a logo of a pentagon surrounded by same-size pentagons, and Penrose started iterating it and augmented the gaps of the pattern by parts obtained by cutting up additional pentagons. Penrose, when he was still a graduate student, had had some interactions with Bernal in the mid-1950s; the story borders the mysterious as Penrose remembered decades later: "He [Bernal] came to see me completely out of the blue, just because he was looking for people who might have ideas, to do with these pentagons, and so on."<sup>[46]</sup>

Mackay took Penrose's effort one step further and produced a simulated electron diffraction pattern of a threedimensional Penrose pattern.<sup>[47]</sup> Mackay warned that if we exclude the possibility of extended structures with five-fold symmetry, we may experience it, yet ignore it.<sup>[48]</sup> Fortunately, this is not how it played out, although it could have.

In 1982, at the then National Bureau of Standards, Dan Shechtman (Figure 32), a visiting scientist from the Technion, was experimenting with electron diffraction of a great variety of manganese-aluminum alloys. He obtained a diffraction pattern that could be interpreted as an extended structure of ten-fold symmetry – clearly "in violation" of the rules of classical crystallography.<sup>[49]</sup> When the experimental observation was properly documented, it turned out that there was instant theoretical interpretation and even a catchy name for this new state of matter.<sup>[50]</sup> Shechtman's perseverance brought this discovery to triumph, but not before he had to face the dis-



**Figure 32.** In 1984, at NBS, from left to right: Dan Shechtman; Frank Biancaniello; Denis Gratias; John Cahn; Leonid Bendersky; and Robert Schaefer. Photograph by H. Mark Helfer/NIST; courtesy of NIST. Biancaniello prepared the alloy samples and created a broad range of allowed compositions. John Cahn and Dennis Gratias were two of Shechtman's three co-authors on his seminal paper reporting the discovery.

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belief, and even ridicule, of establishment scientists. The story has been well documented by several authors, including the present one.<sup>[51]</sup>

In this case, it was not the ambiguity of a concept, but the ambiguity of the scope and definition of classical crystallography that was what had to be sorted out. It was not trivial though. We have seen above how innovative Linus Pauling could be in breaking down previous dogmas in his quest for the alpha helix. Decades later, he could not accept Shechtman's breaking down some other dogmas. Planck's words come to mind about the new ideas that keep appearing in science and that even great old scientists find unable to accept: "An important scientific innovation rarely makes its way by gradually winning over and converting its opponents: it rarely happens that Saul becomes Paul. What does happen is that its opponents gradually die out, and that the growing generation is familiarized with the ideas from the beginning."<sup>[52]</sup>

#### 6. Chirality

This contribution is for a special issue in the Israel Journal of Chemistry honoring the fiftieth anniversary of the first successful chiral column separation of racemic amino acids by the late Emanuel Gil-Av of the Weizmann Institute. Chirality plays a fundamental role in many chemical events, while, according to Weinberg, "chiral symmetries ... are not fundamental symmetries underlying the laws of nature."<sup>[53]</sup> For the importance of differences in the properties of chiral pairs of molecular substances, suffice it to mention the thalidomide story. It had many more tragic consequences in Western Europe in the 1950s than in the United States. The difference was primarily due to an officer at the Food and Drug Administration, Frances O. Kelsey (Figure 33), who was not satisfied with the knowledge about the substance enough to give it the green light to the US market. As it turned out, in the enantiomeric mixture of thalidomide, one enantiomer was teratogenic, the other was not (but even that transformed into the teratogenic isomer in the organism). For some time now, legislation has mandated that only enantiomerically pure pharmaceuticals can be marketed.

Yet another scientist to mention here is Vladimir Prelog, one of the founders of modern stereochemistry. His office at the Eidgenössische Technische Hochschule Zürich (Swiss Federal Institute of Technology in Zurich) was full of memorabilia of stereochemistry and chirality, in particular. His *ex libris* was a drawing by Hans Erni, which has become well known all over the world (Figure 34). Prelog chose this drawing, because it represented all the paraphernalia that describe chirality: human intelligence, a left and a right hand, and two enantiomorphous tetrahedra. Erni prepared more than one version of this drawing, but the one Prelog chose for his books was peculiar. The two hands appear as if they are



**Figure 33.** Frances O. Kelsey in 2000 in her office at the Food and Drug Administration in Rockville, MD (photograph by and courtesy of Magdolna Hargittai).



**Figure 34.** Vladimir Prelog's *ex libris* plate by Hans Erni with Prelog's dedication to the author (courtesy of the late Vladimir Prelog).

turned around, inverted, as can be imagined as a consequence of the two arms being crossed.<sup>[54]</sup> Other versions of Erni's drawing were displayed in Prelog's office with the two hands being non-inverted, parallel. Further examples of pairs of hands appear in Figures 35 and 36.

Chirality may not be a fundamental property underlying the laws of nature, yet it has vital consequences for our lives and for life in general. It intrigued Lewis Carroll's *Alice* when she asked a question deep-rooted in chirality (Figure 37). In the book, *Through the Looking Glass*, comparison of an image and its mirror reflection makes Alice wonder, "Perhaps Looking-glass milk is not good to drink ..."<sup>[55]</sup> Some time ago, in a brief paper titled *Eternal dissymmetry*, we summarized some examples that illustrate how "the teachings of Louis Pasteur about chirality continue to instruct and inspire."<sup>[56]</sup>



**Figure 35.** Heterochiral pair of hands in the old Jewish cemetery in Prague (photograph by I. Hargittai).



**Figure 36.** Homochiral pair of hands, "The Cathedral," by Auguste Rodin in the Rodin Museum in Paris (photograph by and courtesy of Magdolna Hargittai).

#### 7. Conclusion

Ambiguity of symmetry impacts the validity of the symmetry concept and its applicability. Take, for example, molecular structure. Information about its symmetry is always interesting, often useful, and sometimes crucial. The reliability of the determination of molecular symmetry increases with increasing molecular rigidity and fluxional behavior enhances its ambiguity. Ambiguity may also exist in our various definitions, as it turned out, for example, for the one used to define what a crystal is. The old definition had to be replaced by a more inclusive one following the discovery of quasicrystals. The more comprehensive definition has rendered the label quasicrystal a misnomer or at least superfluous; nonetheless, its usage has continued without causing any misunderstanding.

Another aspect of ambiguity is when perfect symmetry is damaged – is symmetry still there? The expression per-



**Figure 37.** Sculptural group "'Curiouser and curiouser!' cried Alice" (by Jose de Creeft, 1959) in Central Park, near the Conservatory Lake (76<sup>th</sup> Street and Fifth Avenue), New York City, 2015 (photograph by I. Hargittai).

fect symmetry does not make sense in a rigorously geometrical sense. There is symmetry or there is not. However, in real systems, this is not the way we handle symmetry, and in real systems, the ambiguity may develop into arbitrariness. In other words, it depends on our tolerance – some times on our goodwill – whether we continue to consider something symmetrical, whereas it no longer is, according to stronger criteria.

Take, for example, the sphere whose simple figure possesses an infinite number of symmetries and about which Copernicus wrote: "... the spherical is the form of all forms most perfect, having need of no articulation; and the spherical is the form of greatest volumetric capacity, best able to contain and circumscribe all else; and all the separated parts of the world – I mean the sun, the moon, and the stars – are observed to have spherical form; and all things tend to limit themselves under this form – as appears in drops of water and other liquids – whenever of themselves they tend to limit themselves. So no one may doubt that the spherical is the form of the world, the divine body."<sup>[57]</sup>

For thirty years, Fritz Koenig's 7.6-meter metallic sculpture "The Sphere" graced the plaza at the World Trade Center (Figure 38). It was not a perfect sphere in the geometrical sense, and it did not have all the symmetry elements of the sphere in the rigorous geometrical sense, yet nobody doubted its being a sphere. It symbolized world peace through world trade. The terror attack on September 11, 2001, badly damaged this sculpture. Defiance and resilience reconstructed the sculpture from its salvaged remains, and now it honors the victims of the terror attack. In this disfigured version, "The Sphere" has lost none of its grace and nobody has any problem in identifying it as being a sphere. Its sculptor noted its transforma-







**Figure 39.** The sculpture-turned-monument in Battery Park, Manhattan, Fall 2014 (photograph by I. Hargittai).

tion from being a sculpture to becoming a monument (Figure 39).<sup>[58]</sup>

There is a steady extension of our knowledge of materials, including systems under extreme conditions (created on our planet or existing in space), many of them disordered or partially disordered. Many others may yet emerge. Structural variations of the building blocks of living organisms have also expanded the scope of science about structures. We have learned to live with ambiguities and we are learning to value ambiguities in symmetry and elsewhere.

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