Consequences of Expanding Chirality to Include Spin Isomery (The Dilemma of Broadening Chirality into Handedness)

Radu Popa

Portland State University, Portland, OR, 97201, USA.

e-mail: rpopa@pdx.edu

Vily Marius Cimpoiasu, Romulus Ion Scorei

University of Craiova, Craiova, Romania.

Abstract

We analyzed the motivation and consequences (i.e. benefits and pitfalls) of expanding chirality to include spin isomers, non-space dimensions and arbitrary number of dimensions. The prevailing opinion in the literature is that "Chirality" should remain restricted to objects constructed in four architectural dimensions and to mirror images, and be described as a particular example of "Handedness". Handedness is more comprehensive, can include any type of dimension, and appears relative because the number of symmetric states depends on the difference between the number of liberties of the observed and those of the observer. For example in a simpler $2D$ world four types of glycine exist (two of them are symmetrical and handed). This makes glycine non-handed in a $3D$ world but some projections of it are handed in a $2D$ world. Both, chirality and handedness remain restricted to two symmetrical liberties on each dimension. To the question of whether some complex forms of spin isomers (such as $H_2^{17}O$) can be included in handedness the answer is: "not fully". It is not because spin isomers are not complex enough to be handed, but because AAX spin isomery includes some states that are handed and others that are not. A generalization of chirality into handedness is useful to analyze state pairs in new dimensions and to better understand the transfer of asymmetry from various forms of handed objects to chirality.

1   Introduction

When objects constructed in four independent architectural dimensions are analyzed in a $3D$ space the additional constructive liberty allows the existence of two states that are similar in composition yet different in organization. Chirality is present when these states are perfectly mirror symmetric but cannot be superimposed in real world (in chemistry these states are known as enantiomers). Diastereoisomery occurs when two such states are similar in composition but are not mirror symmetric (in chemistry these states are called diastereoisomers). For a number of reasons efforts were made to broaden the meaning of chirality to include more than chemical structures and geometrical objects; these efforts took different avenues. Helicity uses the direction of the transition between different space

directions as a fourth non-orthogonal dimension [1]. Physical chirality (or chiral motion) resembles helicity and uses behavior relative to time as the fourth independent dimension [2][3]. Analysis of chirality in an arbitrary number of dimensions was also proposed [4]. Chirality may be seen as one of the particular cases of *"isomery with discontinuous liberties"* (i.e. based on discrete choices); this interpretation allows subjecting chirality to a information theory analysis [5]. Adding different isotopes to some molecular structures (i.e. creating isotopomers) can also result in chirality [6][7][8][9]. Extrapolations may also be made from spin-isomery (or spinomery) [10] toward a possible chiral spinomery. Some complex electromagnetic organizations and subatomic behavior are sometimes portrayed as chiral [11]; yet, they are seldom embraced by classical chirality because subatomic entities and effects are seen as ephemeral or transitory states, fields are continuous (rather than offering discrete alternatives) and many of the chirality-related terms (for example enantiomers, racemic state, enantiomeric excess, racemization, etc.) are not common in the subatomic-level and field-level vocabulary.

In the conventional sense chirality is generalized as a particular example of isomery, and chiral objects or effects only occur when two non-superimposable forms are inter-convertible by parity symmetry (i.e. P-symmetry with left and right swapped) or by time reversal (T-symmetry or reversal of motion). Is it appropriate or useful to broaden the concept of chirality?

Subtle differences were found between enantiomers regarding solubility [12][13], magnetic properties of crystals [14], crystallization in metal-rich complexes [15], and chemical reactivity [16][17][18]. These differences are contrary to chiral symmetry expectations, they do not seem to come from other chiral structures of chiral effects or from energy dissipation and cannot be explained by Parity Violation Energy Differences [19][20][21]. It was proposed that such asymmetric effects may start from ring currents in chiral centers [22][23], neutral currents in weak interactions [24], changes in charge distribution of chiral centers when placed in magnetic fields (**B**) [25], differences in *ortho:para* organization [26], and asymmetric interactions of enantiomers with complex nuclear spin-isomers such as $H_2^{17}O$ [17]. Is it correct to say that the asymmetry of chirality present at the nuclear spin-level produces asymmetry in the chirality present at the chemical level? One obvious dilemma with spin-isomers is that they are not easily included in "classical chirality", which is seen by most scholars as a purely geometrical concept or time reversal symmetry [3]. Furthermore, although some homologies can be found between chirality and spin-isomery, classical chirality's specialized terminology (see above) is not used in nuclear chemistry. Handedness on the other hand is a broader concept than chirality; it includes chemical chirality and applies to any type of phenomena and structures; for example: chemical chirality, symmetrical motion and behavior, circularly polarized light, energy dissipation, combinations of different forces, actions, fields and objects [3][27][28][29][30]. Handedness includes properties that are homologous to chirality's vocabulary; for example: symmetry, asymmetry, level of statistic or thermodynamic equilibrium and rate of change toward or away from equilibrium. One small lexical problem is that by tradition most scientific terminology is derived from Greek or Latin, while the word "handedness" is in English and its Greek derivatization is "chirality". If we can ignore this vocabulary slippage we are free to explore the liberties of "handedness" not shackled by restrictions of classical chirality. Do we need to broaden the term chirality or is it simpler to use Handedness for analyzing how chiral asymmetry may arise from non-chiral "things"? Is "handedness" truly broader than chirality? What features can be tolerated in "handedness" but do not belong with classical chirality? Here we discuss the particular example of nuclear spins.
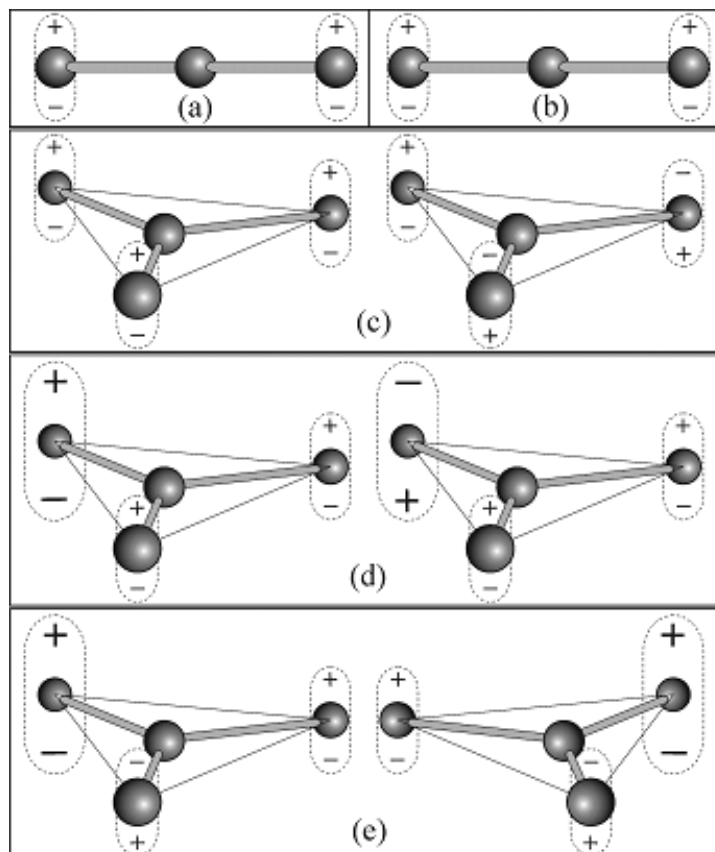
Figure 1: Example of distributions of two and three electrical fields in abstract chemical structures. These fields are considered distant enough not to influence each other's overall orientation and behave as independent alternatives. (a) Two parallel fields similar in magnitude (A↑↑A). (b) Two antiparallel fields (A↑↓A). (c) Three similar fields in two different organizations; these states are not identical upon space reversal and are analogous to diastereoisomers. (d) Three fields, two similar and one dissimilar in magnitude (AAB) with A↑↑A in two arrangements, also resembling diastereostructures. (e) Three fields (AAB) with A↑↓A. Unlike all organizations shown above the two (e) organizations are homologous to enantiomers (thus handed) and will exist in two non-superimposable mirror images.

2   Discussions

2.1   Handedness

Concept#1. Unlike classical chirality handedness extends beyond substance to include the organization of fields as well. Figure 1 gives examples of organization of electrical fields in different spatial arrangements.

Concept#2. Also seen in Figure 1 is the fact that handedness (i.e. chiral state in chemistry) is a state occurring spontaneously during increase in complexity. Some structures are too simple to display handedness or chirality. The best known example from biochemistry is among amino acids where glycine is too simple to be chiral while all other amino acids are chiral. Glycine can be reduced to three architectural directions while all other amino acids have four different chemical groups around the chiral center. When glycine is attached to a surface (a world in which only two translational and one rotational
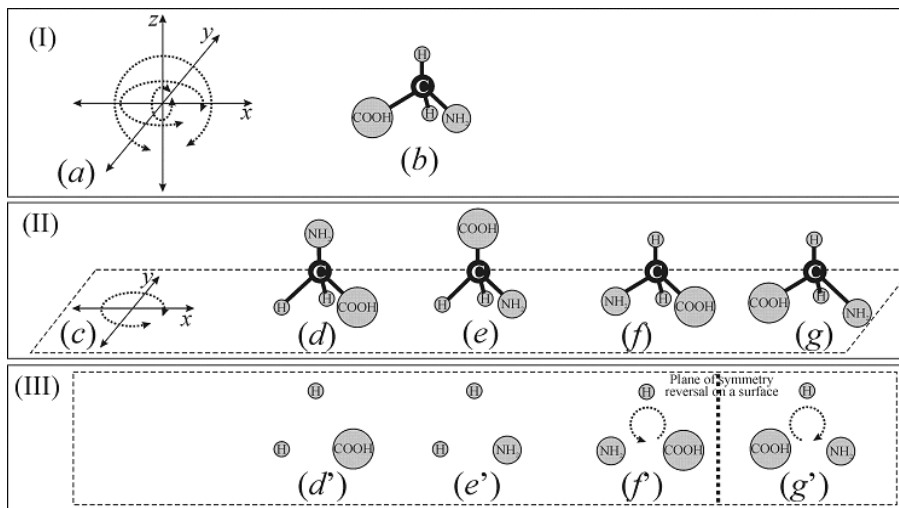
Figure 2: The amino acid glycine (b) is achiral in a *3D* world (panel I) but may exist in two handed orientation in a *2D* world (i.e. when attached on a surface). (Ia) In a *3D* space three liberties of translation and three liberties of organization exist, while on a surface (IIc) only two liberties of translation and one of rotation are possible. When glycine is attached to a surface four orientations are possible having three points of contact with the surface (II,d,e,f and g) corresponding to the four faces of the (b) tetrahedron. (III) The plane from Panel II seen from above and showing the orientation of the chemical groups of glycine attached to the surface. Two of these space distributions (f' and g') have opposite orientations of the $COOH - NH_2 - H$ sequence, one that is counterclockwise (f') and the other clockwise (g'). Because flipping across the plane is not possible in a *2D* world (c), the equivalent of mirror imaging in a *2D* world is pasting the distribution across a symmetry reference line situated on the x,y plane. Thus in a *2D* world (II) the (f' and g') orientations are handed and analogous to enantiomers from a *3D* world.

liberties are possible), four orientations with three points of contact to the surface are possible (Figure 2). Restricted to the rotational and translational liberties allowed on a surface two of these orientations are non-overlapping and symmetrical distributions, analogous to enantiomers from a *3D* world. This suggest that: (a) some structures that are not complex enough to be chiral in a *3D* world may result in handedness in a less complex reference framework; and (b) in a *2D* world the equivalent of mirror imaging is the graphical "pasting" of a distribution across a "symmetry reference line" situated on the xy plane (Figure 2). This requires discussing the relationship between handedness, space dimensions and complexity as well as reconsidering the concept of mirror as means of defining handedness in worlds with arbitrary number of dimensions.

We learn a couple of important lessons from the Figures 1 and 2:

(a) Chirality (and by extension handedness) is a state related to the level of complexity. The relationship between the number of liberties of a system and the number of liberties of analysis defines what is handed and what is not (Figure 3);

(b) In systems with multiple dimensions many handed pairs are possible based on the various combinations of liberties we use for analysis and based on the dimensions considered for reversal;

(c) In agreement with Arnaut (1997) [4] the concept of handedness expands to an arbitrary number of dimensions; this is more comfortable to those restricting chirality to
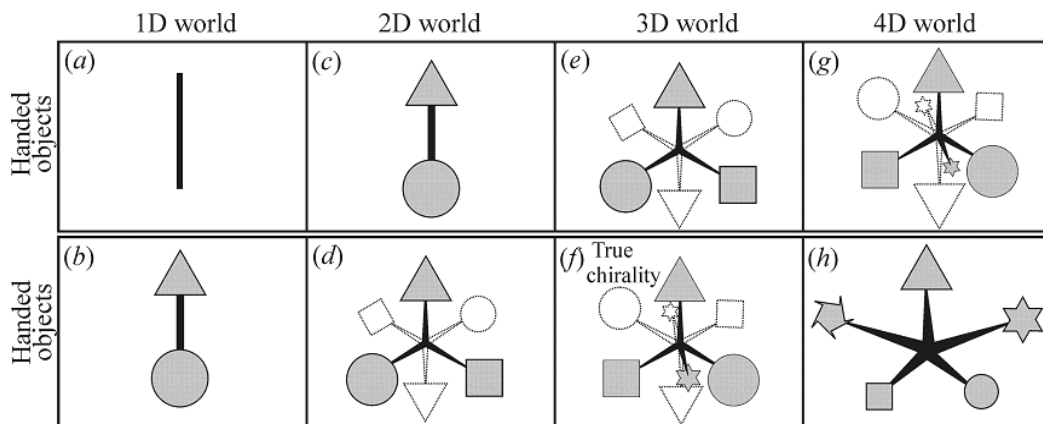
Figure 3: Handedness is a property dependent on the difference between the number of liberties of a construct and the number of external dimensions or the number of liberties of the observer. The object from (f) is analogous to a chemical tetrahedron with four types of radicals distributed around a central atom; this object is chiral in a *3D* world. If the architecture of (f) is simplified to a three dimensions construct (e) then it becomes non chiral in a *3D* world. If (e) is brought in a *2D* world then two symmetrical arrangements of it may exist (i.e. clockwise and counterclockwise). These arrangements cannot overlap each other because in a *2D* world flipping across the z axis is not possible. Similarly, if the object from (c) is analyzed in a *1D* world, then two forms are possible because here only translation (and no rotation) is allowed. A reciprocal interpretation can be given toward higher dimensions worlds, in which (f) becomes achiral because in higher dimension worlds more liberties of translation and rotation are permitted possible. (h) To create a handed object in a *4D* world the analyzed object has to carry five liberties.

P- or T-symmetry; and

  d) When handedness contains only discrete alternatives it is similar to independent system states analyzed by the theory of information.

  Concept#3. Handedness extends beyond space and time dimensions and includes any properties with discrete, independent and opposite alternatives that become similar upon reversal (Figure 4).

2.2   Spin isomery

  Based on the above, can we find examples of handedness in complex spin isomers? If yes, can asymmetry from this handedness also influence chiral asymmetry?

  Nuclear spin-isomery is known for a long time [31][32][33][34]. When two magnetically equivalent nuclear spins such as ^1H and ^1H (from H_2 or H_2O) are close they become coupled in four states, three *ortho* $\left(\alpha\alpha; \beta\beta; \left(1/\sqrt{2}\left(\alpha\beta + \beta\alpha\right)\right)\right)$ and one *para* $\left(1/\sqrt{2}\left(\alpha\beta - \beta\alpha\right)\right)$. These four states are not fully symmetrical and thus cannot be all interpreted as being handed. A graphical representation is given in Figure 5. Some of these pairs are subatomic equivalents of mirror-dissimilar structures. Yet, from the point of view of magnetic moment individual nuclear spins and the *ortho* pairs have two mirror image opposites. This allows describing them as true isomers [26]. Because spin orientation is independent of the spatial orientation of a molecule, nuclear spin orientations, and *ortho* and *para* configurations of H_2O have no steric consequences when water molecules are free to rotate in solution. The addition of an external magnetic field (**B**) and the immobilization of molecules on surfaces results in organization with the *ortho* pairs or
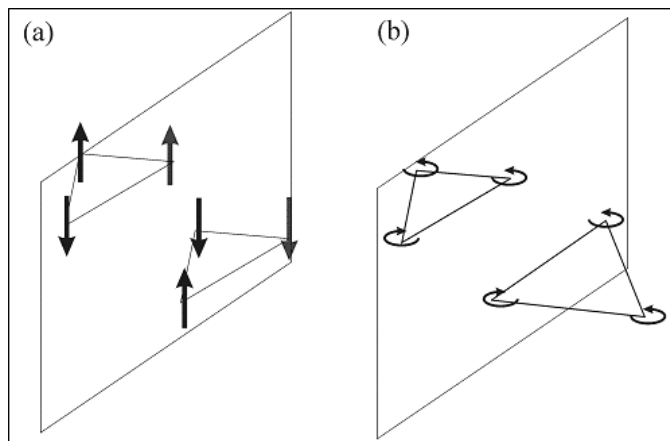
Figure 4: Any type of reference (dimension) is tolerated in handedness. Examples include fields or direction of rotation.
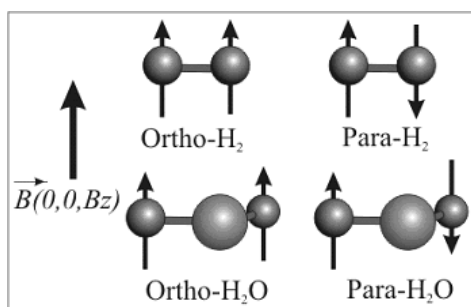

Figure 5: In the presence of an external **B** aligning two interacting nuclear spins relative to each other and to **B**, hydrogen and water molecules have two groups of spin architectures: ortho and para. These configurations are spin isomers but too simple to be analogous to enantiomers.

the individual spins having magnetic moments aligned parallel or antiparalel to **B**. The magnetic field in this case is the fourth dimension.

More complex nuclear spin isomers are created by the presence of atoms with nuclear spins to simpler spin isomers. Examples of ortho-based spin isomers are shown in Figure 6.

Because spin alignments are largely independent of the spatial orientation of a molecule, and can be either parallel or antiparallel relative to **B**, this form of organization adds one more degree of liberty to the system. In this case **B** represents the fourth external orthogonal reference dimension. Obviously, when the spin:spin B alignment degree of freedom is added to H_2 it does not result in a structure analogous to chirality because H_2 is not complex enough relative to our *3D* world. For handedness to exist the total number of liberties of the observed system has to exceed the number of liberties of the observer by at least one.

3   Conclusions

We analyzed the motivation and consequences (i.e. benefits and pitfalls) of expanding chirality to include spin isomers, non-space dimensions and arbitrary number of dimen-
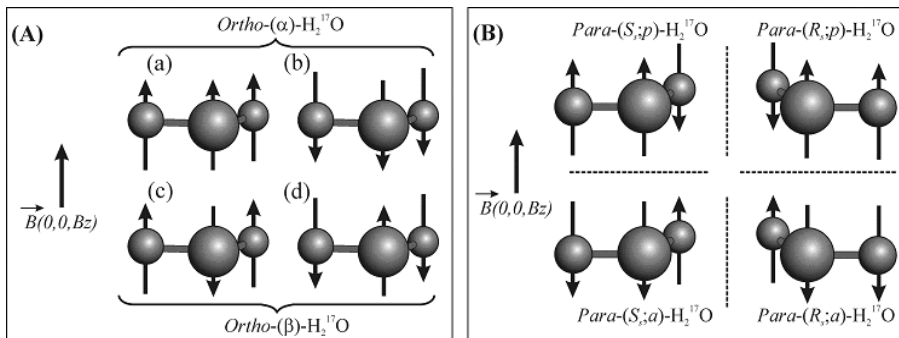
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Figure 6: (A) When the spatial orientation of the HOH plane of $H_2^{17}O$ is non-parallel with $\mathbf{B}$, and $^1H \uparrow\uparrow^1 H$ two types of $H_2^{17}O$ spinomers will exist (α) and (β). In the α forms [(a) and (b)] the spin of 17O is parallel with the orientation of the hydrogen spins, while the β forms [(c) and (d)] are the antiparallel alternatives. The configurations from panel A cannot be handed. (B) When $^1H \uparrow\downarrow^1 H$ four spinomers of $H_2^{17}O$ can be described: $S_s(p), S_s(a), R_s(p)$ and $R_s(a)$. The nuclear spin ^{17}O may be either parallel or antiparallel with $\mathbf{B}$ (here the abbreviations (p) for parallel and (a) for antiparallel are used). The $H_2^{17}O$ spinomers from panel (B) are complex enough to show four handed pairs because mirror imaging can be performed relative to two types of independent dimensions (one spatial and one relative to the direction of B). The S_p/R_p pair and the Sa/Ra pair are mirror image opposites if the direction of $\mathbf{B}$ is considered homologous to a spatial orientation and the mirror image is produced relative to one of the spatial dimensions. The S_p/S_a pair and the R_p/R_a pair are mirror image opposites and handed when we create mirror images relative to $\mathbf{B}$.

sions. It is obvious that many *"handed features"* exist in nature with symmetric alternatives vis a vis liberties that are not typically analyzed by chirality (i.e. space and time). Such *"handed features"* have attributes resembling properties of chirality (such as: enantiomers, departure from mirror symmetry, symmetry breaking and racemization); though this vocabulary is inappropriate outside chemistry. Because of this homology and because the asymmetry of such *"handed features"* may influence chiral equilibrium some scholars felt attracted to broaden the meaning of chirality. In practice the word chirality (and its vocabulary) remains restricted to P and T symmetry, and resilience will always exist against any chiral broadening.

The prevailing opinion is that "Chirality" should be restricted to objects constructed in four architectural dimensions and to mirror images, and should be classified as a particular case of *"Handedness"*. Handedness has the quality that it can include any kind and number of dimensions. The obvious problems with the word "Handedness" are its lack of rooting in Greek or Latin and that its nearest translation in Greek is actually "Chirality". No satisfactory solution yet exists to this problem, which remains a *status quo* almost useless to try budge. The general feeling is that if the motivation, consequences and theoretical principles of handedness and chirality are correctly appraised there is little need to push for finding another proper name. Chirality remains restricted to objects with four liberty axes and PT symmetry in a *3D* world, while all other features (spins, fields and arbitrary number of dimensions) can be described as "Handedness". Chirality and Handedness only occur at certain levels of complexity. Handedness appears to be a relative property because the number of symmetric states will depend on the difference between the number of liberties of the observed and those of the observer. Presently,

both, chirality and handedness remain restricted to two symmetrical liberties relative to each dimension. To the question of whether some complex forms of spin isomers (such as those of $H_2^{17}O$) can be included in handedness the answer is … "Not fully". Surprisingly, this is not because spin isomers are not complex enough to be handed. The AAX spin isomery includes both handed and non-handed states. Regarding the transfer of asymmetry across different *"handed features"*; if the 2nd law of thermodynamics is obeyed, any source of symmetry disruption (chirality included) has to be rooted in another source of asymmetry at least as large as itself, or asymmetric work has to be done on the system with corresponding dissipation of entropy.

4   Acknowledgments

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