

Mathematical Patterns in Chemistry – on Turn Points in the Molecular Self-Assemblage Symmetry Formation

Lech P. Schulz

Department of Chemistry, Adam Mickiewicz University, Poznan, Poland
(E-mail: lsch@artemida.amu.edu.pl)

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Abstract. Does the abstract mathematics afford patterns for chemistry? It is supposed that mathematics has its own, autonomous criteria of development and that mathematical creativity cannot be progressed simply by a "blind" listing of possible tautologies. Simultaneously, applied findings in the independently developed mathematical areas are rather a rare case. In the present work, it has been shown that seemingly abstract and presumed not to have any direct application concepts of pure mathematics lead to the concrete entities encountered in chemistry. For these reasons, the general definition of molecular forms and mathematical atoms have been employed to derive objects corresponding to the basic particles of chemistry. Besides, using a pattern of foundations of arithmetic, a special relation has been found to determine such atomic species in some chemical categories. The arithmetical background of chemistry and possible extensions have been indicated in this way.

Keywords: atom, self-assemblage chemical space, self-organization, molecular form

INTRODUCTION

On the General Mathematical Notion of an Atom

Tendencies observed in applied natural sciences are commonly focused on the usage of well established mathematical techniques and they rather avoid insights in the grounds of the employed knowledge. This gap is especially well seen, *e.g.*, in computer modeling, which commonly prevails over a mathematical and experimental bottom. Rare initiatives¹ insisting on the recognition of sources of the results received inspire providing a means for better understanding of matter surrounding us. This is not only a question of cognitive scientific interest but a vital problem of real progress in eliciting reliable information on molecular structures.

A kinship between arithmetical foundations of mathematics and chemistry leads to the conjecture that an exploration of relevant, widely applicable mathematical findings can reveal traces to quite novel concepts regarding structural features of molecules. The idea of mathematical chemistry,¹ as a part of mathematical natural sciences, assumes the existence of specific dependencies between contents of abstract mathematics and related physico-chemical reality. An aspect stressed in this study is a usage of mathematics as a source of

information on the systems of interest instead of treating it as a tool only. Thence, the leading motto pursued hereinafter involves a correspondence pictured below.

Due to the goal outlined, a more detailed insight is necessary in mathematical subject pointed out in the diagram of Figure 1. Let simple examples illustrate further generalizations. Consider the *one-element set* $\{x\}$ also called a unit set or singleton [The term "element" is exclusively used herein in the mathematical sense]. Such a set cannot be partitioned in non-empty subsets

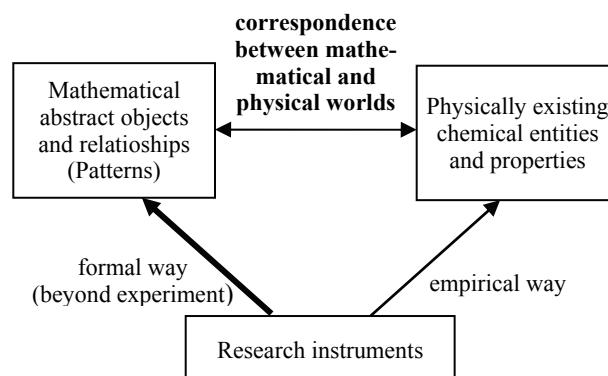


Figure 1.

and therefore it deserves the name of an *atom* due to its Greek origin. Let the underlying set A consist of three elements, *i.e.*, $A = \{0, 1, 2\}$. Then, an easy task is to determine the *power set* of A consisting of all subsets of A .

$$\text{Pow}A = \{\emptyset, \{0\}, \{1\}, \{2\}, \{0,1\}, \{0,2\}, \{1,2\}, \{0,1,2\}\} \quad (1)$$

Elementary operations on the subsets (1) are *intersection* (denoted \cap), *union* (\cup), *subtraction or difference* (\setminus), and *symmetric difference* of sets (Δ). In particular,

$$\begin{aligned} \{0,2\} \cap \{0,1,2\} &= \{0,2\}, \{0,1\} \cup \{1,2\} = \{0,1,2\}, \\ \{0,1,2\} \setminus \{1\} &= \{0,2\}, \{0,1\} \Delta \{0,2\} = \{1,2\} \end{aligned} \quad (2)$$

Relations between elements of a set can be distinguished in various ways. *e.g.*, define the *relation of equipollence* in $\text{Pow}A$.

$$r = \{(a,b) \in \text{Pow}A \times \text{Pow}A \mid \text{cardinality of } a \text{ equals cardinality of } b\} \quad (3)$$

The *ordered pair* (a,b) fulfils a relation r simply if (a,b) belongs to r (often denoted arb for short). The relation (3) is an *equivalence*, *i.e.*, it is reflexive, symmetric and transitive. Owing to this fact, the equipollence (3) divides set $\text{Pow}A$ in disjoint *equivalence classes* covering it [The terms "class" and "set" are synonyms in this paper]. The set of such classes is called a *quotient set* (under fixed relation r).

$$\text{Pow}A / r = \{\{\emptyset\}, \{\{0\}, \{1\}, \{2\}\}, \{\{0,1\}, \{0,2\}, \{1,2\}\}, \{\{0,1,2\}\}\} \quad (4)$$

One can easily find subclasses *consistent* with the power set (4) along with some distinguished operations. This means that the operations considered, *e.g.*, symmetric difference and intersection, result in sets belonging to this class. It is said that a subclass of (4) is *closed* under these operations. For example, the singleton $\{\emptyset\}$ including only the empty (null) set is such one or the class

$$\mathcal{E} = \{\emptyset, \{0\}, \{1\}, \{0,1\}\} \quad (5)$$

has the required property. The equivalence class $\{\{0,1\}, \{0,2\}, \{1,2\}\}$ of (4) is not consistent in the sense just mentioned. The three

$$(\text{Pow}A, \Delta, \cap) \quad (6)$$

constitutes an algebraic ring, where the role of a unit plays the whole set A . If the subclass \mathcal{E}' of $\text{Pow}A$ is consistent with $(\text{Pow}A, \Delta, \cap)$, then the 3-tuple

$$(\mathcal{E}', \Delta', \cap') \quad (7)$$

with restricted symmetric difference and intersection is also a ring, and it is called a *subobject* of $(\text{Pow}A, \Delta, \cap)$. Subobjects are often identified with the consistent subsets.

A naturally occurring relation in $\text{Pow}A$, different from the equipollence (3), is the relation of inclusion.

$$r =: \subseteq_{\text{Pow}A} = \{(\emptyset, \{0\}), \dots, (\{0\}, \{0\}), (\{0\}, \{0,1\}), \dots, (\{1,2\}, \{0,1,2\})\} \quad (8)$$

An *inversion* of the relation (8) is the set of reversed pairs. Observe that the empty set is included in every class of $\text{Pow}A$. An element a related by the relation r to all elements of A different from a is called the *first (smallest, least) element*. For example,

$$\text{Fe}(\text{Pow}A, \subseteq_{\text{Pow}A}) = \{\emptyset\} \quad (9)$$

though this is not true for the inversion of relation (8). Unit sets like $\{0\}$ or $\{1\}$ are not the first elements in $\text{Pow}A$ but they are minimal since there exists no non-empty subset of A included, *e.g.*, in the set $\{0\}$, and different from it. Thus, a set of *minimal elements* can be determined.

$$\text{Min}(\text{Pow}A \setminus \{\emptyset\}, \subseteq_{\text{Pow}A \setminus \{\emptyset\}}) = \{\{0\}, \{1\}, \{2\}\} \quad (10)$$

This is well seen that minimal elements have been distinguished amongst non-empty subsets of A by means of the relation (8) reduced to the same subsets.

Yet one property is worth mentioning. This is easy to check that only the set consistent with the ring (6) and embracing $\{\{0\}, \{1\}, \{2\}\}$ equals $\text{Pow}A$. Similarly, the smallest set consistent with the same ring and embracing $\{\{0\}, \{1\}\}$ is the set (5). It is said that $\{\{0\}, \{1\}, \{2\}\}$ or $\{\{0\}, \{1\}\}$ generate respective rings, *i.e.*,

$$-\{\{0\}, \{1\}, \{2\}\} = \text{Pow}A, \quad -\{\{0\}, \{1\}\} = \mathcal{E} \quad (11)$$

Consider the same in more general terms. In mathematics, the term *atom* crops up on the occasion of distinguishing certain elements of *Boolean algebras* sometimes called *Boolean rings* (with or without a unit). A Boolean ring is a commutative ring with the idempotent "multiplication" (*i.e.*, $x \cap x = x$). Let A be an infinite set. Then the finite subsets of A constitute a Boolean ring.

$$\begin{aligned} \mathcal{A} &= \{a \subseteq A \mid a \text{ is finite}\}, \\ X &= (\mathcal{A}, \Delta, \cap) - \text{Boolean ring} \end{aligned} \quad (12)$$

The relation r by means of which atoms are distinguished is of the following form

$$r =: \{(a,b) \in \mathcal{A} \times \mathcal{A} \mid a \cap b = a\} = \subseteq_{\mathcal{A}} \quad (13)$$

In this case, atoms have been determined as such elements $a \neq \emptyset$ (where \emptyset is the neutral element under "addition" Δ) that whenever the pair (b,a) fulfils the relation (13) and $a \neq b$, then $b = \emptyset$. As the result, the class of singletons of A has been received

$$\text{At}(\mathcal{A}, r) = \{x \mid x \in A\} \quad (14)$$

Since the set of pairs I_A of equal elements (x, x) is an equivalence relation on A like (3), the just distinguished atoms are elements of a quotient set, *i.e.*,

$$A / I_A = \text{At}(\mathcal{A}, r) \quad (15)$$

For an illustration of the role of atoms, let it be notified that the atoms (14) generate the entire ring just considered, *i.e.*,

$$\neg(\text{At}(\mathcal{A}, r)) = \mathcal{A} \quad (16)$$

The closure $\neg(\text{At}(\mathcal{A}, r))$ denotes the smallest Boolean ring in which the set of atoms (14) is included. Boolean rings embracing atoms in question are subclasses of $\text{Pow}A$ closed under symmetric difference and intersection operations. Such subclasses, if nonempty, determine subobjects of the Boolean ring of all subsets of A . In general, the notion of generation (11) will be used in a similar sense in the course of this paper. Depending on the structure used, the smallest set like the closure $\neg(\text{At}(\mathcal{A}, r))$ will be determined within structures and subobjects being currently under consideration. It is also worth notifying an immediate corollary from the just established statements claiming that if class $\mathcal{A}' \subseteq \mathcal{A}$ is closed under the Boolean ring operations and includes the set of atoms (14), then

$$\mathcal{A}' = \mathcal{A} \quad (17)$$

The equality (16) does not hold generally even if sets of atoms would be the same. For example, the ring \mathcal{A} is strongly included in algebra of all subsets of A .

$$\mathcal{A} \subset \text{Pow}A \quad (18)$$

Using the example of Boolean rings, a general definition of atoms has been introduced, in which the underlying set and relation r can be substituted by a choice.

$$\text{At}(\mathcal{A}, r) =: \text{Min}(\mathcal{A} \setminus \text{Fe}(\mathcal{A}, r), r_{\mathcal{A} \setminus \text{Fe}(\mathcal{A}, r)}) \quad (19)$$

Thus, in general, atoms are minimal elements of a fixed set \mathcal{A} (without first elements) distinguished by a relation r restricted to the set indicated in formula (19). The first elements $\text{Fe}(\mathcal{A}, r)$ are the smallest elements of the set \mathcal{A} under the relation r . A generalization is justifiable, if for example, it broadens the scope of applicability of the modified term. Therefore, an efficiency of the generalization introduced has been tested.

Consider the *relational lattice* $X =: (N, |)$ of integral non-negative numbers (under the relation of divisibility). Atoms of such a relational system are prime natural numbers.

$$\text{Fe}(N, |) = \{1\} \quad (20)$$

$$\text{At}(N, |) = \{p \in N \mid p \text{ is a prime number}\} \quad (21)$$

As in the previous case, prime numbers generate the set carrying the structure. In symbols

$$\neg(\text{At}(N, |)) = N \quad (22)$$

Taking atoms in integral domains into account, a more sophisticated case is encountered. Let $X =:$

$(A, +, \cdot)$ be an *integral domain*,² *i.e.*, X is the commutative ring with a unit in which the set of regular elements equals the set A (without null). In details,

$$\text{reg}(A, \cdot) =: \{x \in A \mid \text{if } x \cdot y = x \cdot y', \text{ then } y = y', \text{ for each } y, y' \in A\} \quad (23)$$

Atoms will be looked for by means of the following relation

$$r =: \{(x, y) \in A^* \times A \mid \exists t \in A : t \cdot x = y \ \& \ \neg(x \in \text{Reg}(A, \cdot) \ \& \ \exists t \in \text{iso}(A, \cdot) : t \cdot x = y)\} \quad (24)$$

where the set $\text{Reg}(A, \cdot)$ denotes all regular elements without units, *i.e.*, without the set of invertible elements denoted as $\text{iso}(A, \cdot)$. Finally,

$$\text{Fe}(A, r) = \text{iso}(A, \cdot) \quad (25)$$

and atoms (counterparts of prime natural numbers) are such non-zero and non-invertible elements that any decomposition into two factors involves at least one unit. Formally,

$$\text{At}(A, r) = \{x \in A^* \setminus \text{iso}(A, \cdot) \mid \forall y, z \in A : x = y \cdot z \Rightarrow y \in \text{iso}(A, \cdot) \ \text{or} \ z \in \text{iso}(A, \cdot)\} \quad (26)$$

For example, $2, 3, 1 + \sqrt{5}, 1 - \sqrt{5} \in \text{At}(Z(i\sqrt{5}), r)$ can be indicated as primes in the quadratic ring $Z(i\sqrt{5})$.

Let the *group* (A, \cdot) act on a set S via the operation \bullet (*cf.*, Ref. 2). Then the relation

$$r =: \{(x, y) \in S \times S \mid \text{there exists } t \in A \text{ such that } t \bullet x = y\} \quad (27)$$

determines a class W of subsets of S on which the group acts, *i.e.*,

$$W =: \{a \subseteq S \mid r(a) \subseteq a\} \quad (28)$$

Atoms distinguished by the general prescription (19) turn out to be group orbits.

$$\text{Fe}(W, \subseteq_w) = \{\emptyset\} \quad (29)$$

$$\text{At}(W, \subseteq_w) = \text{orbits of the group } (A, \cdot) \quad (30)$$

Yet another kind of atoms emerges as set collection *constituents*³ determined by means of the *relation of homogeneity*. Define the relation of homogeneity in the power set of E

$$\text{Hom} =: \{(a, b) \in \text{Pow}E \times \text{Pow}E \mid a \cap b \neq \emptyset \Rightarrow a \subseteq b\} \quad (31)$$

If F is a family of subsets of E , then the class \mathcal{W}_F includes subsets of E homogeneous under all sets of F . *E.g.*, unit sets possess such a property. Atoms of \mathcal{W}_F (assuming $F \setminus \{E, \emptyset\} \neq \emptyset$) are elements of a quotient set under the equivalence relation of equal *neighbourhoods*. In symbols:

$$r =: \{(x,y) \in E \times E \mid \text{Nb}(\{x\}, F) = \text{Nb}(\{y\}, F)\} \quad (32)$$

and

$$\text{At}(\mathcal{W}_F, (\subseteq \mathcal{W}_F)^{-1}) = E/r, \quad (33)$$

where $(\subseteq \mathcal{W}_F)^{-1}$ is the inversion of inclusion in the class \mathcal{W}_F . $\text{Nb}(\{x\}, F)$ denotes all sets (neighbourhoods) of F in which the unit set $\{x\}$ is included. Thus, the set of nonempty constituents partitioning set E has been found in this way.

If A is an arbitrary set, then *involutions* are the symmetric permutations of A

$$\text{Inv}A =: \{f \in \text{bij}A \mid f \subseteq f^{-1}\} \quad (34)$$

The atoms of interest will be distinguished by the following relation

$$r =: \{(f, g) \in \text{Inv}A \times \text{Inv}A \mid f \setminus I_A \subseteq g \setminus I_A\} \quad (35)$$

They turn out to be transpositions

$$\text{Fe}(\text{Inv}A, r) = \{I_A\} \quad (36)$$

$$\text{At}(\text{Inv}A, r) = \{\tau \in \text{bij}A \mid \tau \text{ is a transposition}\} \quad (37)$$

It can also be reminded that such atoms generate the whole symmetric group for finite A .

$$\neg(\text{At}(\text{Inv}A, r)) = \text{bij}A \quad (38)$$

Yet, another example reveals *prime ideals* in the ring of integral numbers Z to be atoms (under inverted inclusion) in the set of all principal ideals nZ .²

It is naturally supposed that the list of possible useful atoms distinguished due to the general relationship (19) is not exhausted by the examples shown. But this has been brought to light that abstract atoms in the sense determined by (19) play certain profound role related to the underlying sets and structures in which they have been distinguished. This is often accompanied by generation of the whole set (e.g., of natural numbers with 0) in which mathematical atoms have been selected. Thus, preparing mathematical tools for distinguishing abstract forms of chemical atoms, their role as building "bricks" of molecules will be involved.

ATOMS IN NUMBER AND CHEMICAL CATEGORIES

Since only "bared" sets like (10) without any informative structure emerged previously as atoms, it is of interest to change this situation by finding forms of mathematical atomic species in chemical categories.^{4,5} In looking for reasonable relation to distinguish chemical atoms via prescription (19), a specific arithmeticity of chemistry leads to the basic analogues of chemical and,

e.g., natural numbers.⁶ Chemical numbers can be either composite or prime numbers, similarly as in the arithmetic of positive integral numbers. For example, there are only three prime numbers in HOW-arithmetic based on the reaction of hydrogen oxidation. Even the unique factorization of natural numbers can have its counterpart in chemical numbers. The existence of such an arithmetic and primes has been proved mathematically.⁴ In this arithmetic, any chemical number σ is uniquely expressed by a product of powers of chemical prime numbers, i.e.,

$$\sigma = \sigma_H^1 \cdot \sigma_O^m \cdot \sigma_W^n \quad (39)$$

A close kinship with natural number foundations suggests that finding atoms in basic number categories would elicit a relation by means of which chemical atoms could be distinguished. The structure of a category is not very far from the structure of a group. Simply, in a pair (A, \cdot) , the multiplication is not determined on the whole set $A \times A$. The details on such a treatment of categories have been placed in Appendix I.

Common examples of categories are groups, monoids, groupoids, etc. Semigroups without unit are not categories [Also different terminology can be encountered in which semigroups are called monoids and *vice versa*⁷]. *Category of sets* \mathcal{E}_{ns} consists of *arrows* (morphisms) (B, f, A) such that

$$f: A \rightarrow B, \quad (40)$$

where A, B are sets of a universe called *domain* and *co-domain* respectively. *Objects* in \mathcal{E}_{ns} are of the form (A, I_A, A) . The multiplication is determined in the following way:

$$(C, g, B) \cdot (B, f, A) = (C, g \circ f, A) \quad (41)$$

If *objects* with structures of the form (A, s) and respective *morphisms* (e.g., homomorphisms, homeomorphisms, etc.) are taken into account instead of set domains and co-domains related by mappings in \mathcal{E}_{ns} , then a concrete category, e.g., of monoids, groups or topological spaces arises. Objects of categories play a role of the neutral element of a group. Any nonempty category has some objects.

Let us establish the system

$$X =: (A, o, S), \quad (42)$$

where $o \in A$ is a fixed point and $S: A \rightarrow A$ maps A into A . If $X' =: (A', o', S')$ is an object of this kind and f maps A into A' such that

$$\begin{aligned} f o &= o' \text{ and} \\ f S x &= S' f x, \end{aligned} \quad (43)$$

for each x of A , then the mapping f is regarded as a morphism in the category of mappings and fixed points.

Arrows of this category are three

$$(X', f, X), \quad (44)$$

where f relates the objects X and X' in the way mentioned above.

Similarly to subobjects of a Boolean ring (*cf.*, (7)), there are subobjects of the system (42) determined by such subsets $E \subseteq A$ that

$$o \in E \text{ and } S(E) \subseteq E \quad (45)$$

Now, let the attention be paid to a closure of an arbitrary subset $E_0 \subseteq A$. The smallest set including E_0 and fulfilling conditions (45), in general, does not equal the whole set A similarly as in (18), *i.e.*,

$$\neg(E_0) \subseteq A \quad (46)$$

Distinguish a *subcategory* of the category determined by arrows (44) so that each object of this subcategory would simultaneously be a closure of the unit set $\{o\}$, *i.e.*,

$$\neg\{o\} = A \quad (47)$$

This implies that, if a subset of A fulfils the induction assumptions (45), then it equals the whole set A . Formally,

$$\text{if } o \in E \text{ and } S(E) \subseteq E, \text{ then } E = A \quad (48)$$

Thus, the classical form of the *principle of induction* has been derived by means of certain closures using subobjects appropriate for the structure in question. Owing to the relationships shown, also other structures, *e.g.*, Boolean ring operations can be regarded as the source of specific principles of induction proper to the structures given like the one of (17).

Let $X = (A, o, S)$ be a system in which the principle of induction (48) is fulfilled. Then o is regarded as a fixed point of A and the mapping S is called a *successor*. There are possible a priori four cases:

- i) $o \notin \text{im}S$, S is injective,
- ii) $o \notin \text{im}S$, S is not injective,
- iii) $o \in \text{im}S$, S is injective,
- iv) $o \in \text{im}S$, S is not injective. (49)

The fourth case is impossible, because if values of the successor operation include the fixed point o , then the successor S becomes an injection. The first three cases listed correspond to the main classes of objects in the category just considered. They are pictured below.

The first case simply distinguishes natural numbers, since all *Peano's axioms*³ are fulfilled. The second case distinguishes numbers with a "double" module. The case in Figure 4 illustrates numbers mod m , where

m is a natural number different from 1. In all these cases, the principle of induction is satisfied as expressed in (48). Moreover, if the principle of induction holds in any object of the form (42), then this object is one of the species illustrated by Figures 2–4. Ascribe suitable denotations for the object of Figure 3 as $\text{Mod}(7,8)$ and $\text{Mod}(0,8)$ for the next one.

Objects X, X' fulfilling the principle of induction (48) can be related by a morphism (43) or not. If they are related by such a morphism, say f , then the inverse relation f^{-1} is again a morphism fulfilling the conditions (43) or it is not any morphism. In the first case, f establishes the *isomorphism* of structures considered. The second case establishes the unique surjection onto the codomain of arrow (X', f, X) . For example, the morphism of an object $\text{Mod}(2,10)$ onto the object $\text{Mod}(0,5)$ ($= \text{mod}5$) is the following

$$f: 0 \mapsto 0, 1 \mapsto 1, 2 \mapsto 2, 3 \mapsto 3, \dots, \\ 7 \mapsto 2, \dots, 10 \mapsto 0, 11 \mapsto 1 \quad (50)$$

It turns out that the relation (exactly its inversion in the current case) determined by existence of a morphism between X, X' with excluded isomorphisms selects atoms as quotient objects equivalent to the Galois' fields (*cf.*, Figure 4), *i.e.*, the objects $\text{Mod}(0,p)$, where p is a prime number. In this way, a reasonable link to the previously established atomic species (21) has been found. A mathematically rigorous approach to the cate-

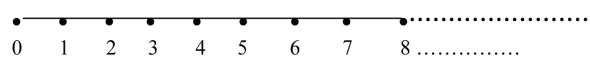


Figure 2. $o \notin \text{im}S$, S – injection.

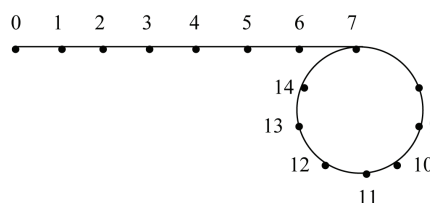


Figure 3. $o \notin \text{im}S$, S is not injection, $S_{14} = S_6$.

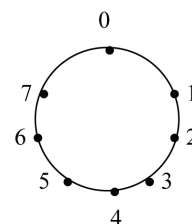


Figure 4. $o \in \text{im}S$, S is injection; $S_7 = 0$ (atoms = Galois' fields).

gories of the kind just described has been entered in Appendix I.

If $\mathcal{C} = (C, \cdot)$ is a category, then bringing what has been just established to notice, the atom distinguishing relation (or its inversion) should be as follows

$$r_e =: \{(a,b) \in \text{obj}\mathcal{C} \times \text{obj}\mathcal{C} \mid \mathcal{C}(a,b) \neq \emptyset = \text{iso}\mathcal{C}(a,b)\}, \quad (51)$$

where $\mathcal{C}(a,b)$ denotes all arrows with the *domain* a and *codomain* b . $\text{iso}\mathcal{C}(a,b)$ are isomorphisms of this kind. In the category of sets \mathcal{E}_{ns} , atoms under relation r_e are the one-element sets (*i.e.*, arrows $(\{x\}, I_{\{x\}}, \{x\})$), as in the Boolean rings or algebras. However, using the principle of induction (48) in categories, objects with structures emerged for the first time as the result of atom selection. On these grounds, having chemical structures, the relation (51) or its inversion is expected to distinguish chemically interpretable mathematical species.

As to the chemical features, the rules of specific molecular self-organization are to be mathematically grounded. Basic chemistry involves the primary stage of self-assembly and a secondary one expressed in forms of *coordination compounds*.⁸ The latter ones include entities of the primary stage (*ligands*) assembled due to strictly determined rules of empirical origin. Using previously established axiomatic system (*cf.*, Appendix II), the central chemical form - a molecule - can be approached from one viewpoint for both stages of self-assembly.

Passing to purely mathematical terms, the 4-tuple (A, λ, ν, \cdot) is such one that λ (called *atomic number operation*) maps A into the set of natural numbers \mathbb{N} (with zero), ν (called *bonding force operation*) is a function with the domain ($\text{dom}\nu$) included in the set of all subsets of A ($\text{Pow}A$) with values in \mathbb{N} , and multiplication \cdot (called *bonding operation*) is a function, which partly maps the Cartesian product of subsets of A into \mathbb{N} (*i.e.*, $\text{dom}\cdot \subseteq \text{Pow}A \times \text{Pow}A$). Endowing this structure with clearly determined and step-by-step dosed information, *self-assembly chemical* (SAC) spaces have been defined with mathematical details (in the form of axioms;⁵ *cf.*, Appendix II). An utmost case does admit the empty set A and the empty operations λ, ν, \cdot . Such an entity is called the *empty space*.

For illustration, an example can be furnished with an anion complex compound called Zeise's salt coordinated by the central platinum atom. A mathematically based ideogram of the respective *SAC space* is given in Figure 5.

SAC spaces are constituted in the way clearly reflecting specific to chemistry auto-organization propensities, which arrange chemical atomic or coordinated species to saturate them. For an element $u \in \text{dom}\nu$, the

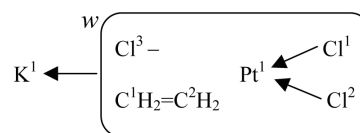


Figure 5. SAC space ideogram of Zeise's salt.

unsaturation is evaluated by the difference

$$\text{usat}u =: \nu u - \text{gra}\partial u, \quad (52)$$

where

$$\text{gra}\partial u =: \sum_{u' \in \text{dom}\nu} \overset{S}{u \cdot u'} \leq \nu u \quad (53)$$

The expression (52) simply shows the number of potential relationships (counted by $\text{gra}\partial u$), which have not been exhausted under species of $\text{dom}\nu$ through the symmetrized bonding operation $\overset{S}{\cdot}$. Let just mentioned operations be specified for the case of Figure 5.

$$\text{Pt}^1 \cdot \text{Cl}^1 = 0, \text{Cl}^1 \cdot \text{Pt}^1 = 1, \text{C}^1 \cdot \text{C}^2 =$$

$$\text{C}^2 \cdot \text{C}^1 = 2, \text{K}^1 \cdot w = 0 < 1 = w \cdot \text{K}^1$$

$$\overset{S}{\text{Pt}^1 \cdot \text{Cl}^1} = 1 = \overset{S}{\text{Cl}^1 \cdot \text{Pt}^1}, \overset{S}{\text{C}^1 \cdot \text{C}^2} =$$

$$\overset{S}{\text{C}^1 \cdot \text{C}^2} = 2, \overset{S}{\text{K}^1 \cdot w} = 1 = \overset{S}{w \cdot \text{K}^1}$$

$$\nu \text{Pt}^1 = \text{gra}\partial \text{Pt}^1 = 2, \nu \text{Cl}^1 =$$

$$\text{gra}\partial \text{Cl}^1 = 1, \nu \text{C}^2 = \text{gra}\partial \text{C}^2 = 4,$$

$$\nu \text{Cl}^3 = 1 > \text{gra}\partial \text{Cl}^3 = 0, \nu w = \text{gra}\partial w = 1 \quad (54)$$

It could be notified that arrows of Figure 5 express only non-commutative algebraic relationships between multiplied elements of the domain of bonding force operation (like $\text{Pt}^1 \cdot \text{Cl}^1 = 0$, $\text{Cl}^1 \cdot \text{Pt}^1 = 1$). Certain insights in potential chemical relevancies are broadly elucidated and discussed in the next section.

An essential feature of chemistry is keeping the whole system saturated, if there are no outer constraints. Formally, this means that the differences (52) should equal 0 for compounds on the primary stage of assembly. Otherwise, such SAC space involves an unsaturation. For example, ethylene $\text{C}^1\text{H}_2=\text{C}^2\text{H}_2$ included as a ligand in the coordination entity w of Figure 5 is saturated while chlorine species Cl^3 is not. The value of unsaturation like

$$\text{usat}\text{Cl}^3 = \nu \text{Cl}^3 - \text{gra}\partial \text{Cl}^3 = 1 \quad (55)$$

is commonly ascribed to the whole *coordination sphere* (*entity*) w and therefore νw equals 1 in the case shown.

So, coordination complexes acquire their bonding force evaluations depending on the saturations of ligands or central atoms (Pt II in the case). Empirical chemists know a precise procedure of such assignments.⁸ This is the point that the whole coordination entity of Figure 5 is regarded as saturated in spite of a ligand unsaturation.

$$\text{usat}w =: \nu w - \text{grad}w = 0 \quad (56)$$

A formal generalized expression of this property can be found in Appendix II. The notion of *saturation (unsaturation)* just considered is different from yet another one used in the sense of existence of multiple relationships between species of the domain of bonding force operation. The above elucidations are necessary for a clear approaching the basic chemical form, *i.e.*, a *molecule*.

A chemical feature met on the way is connectivity. Formally, it is given by a transitive closure of the relation

$$\overset{S}{\cdot} r =: \{(u,w) \in \text{dom} \cdot \mid u \cdot w \neq 0\} \quad (57)$$

In a fixed SAC space, two species $(u,w) \in \text{dom} \cdot$ are connected provided that they fulfill the relation

$\overset{S}{\cdot} (r)^n$ for some natural number n . A classification (Table 1) of the structures considered can be given on these grounds.

To summarize, the objects of chemical categories are *molecules (Mol)*, *molecular spaces (Msp)*, *infra-molecules (IMol)*, and *infra-molecular spaces (IMsp)*. This classification is due to the condition of connectivity and difference between values of the bonding force operation (νu) and self-assembly grades ($\text{grad}u$) in the sense of saturation (unsaturation) aforesaid. Thus, the connectivity obligatorily holds in molecules and infra-molecules as opposed to the molecular and infra-molecular spaces. On the other hand, the saturation mentioned is the case in the sense established for molecules and molecular spaces while for infra-molecules and infra-molecular spaces the difference mentioned has

a non-zero value at least one time for non-ligands or coordination species. Formal details can be found in Appendix II (*cf.*, Table 1').

Let two kinds of morphisms be taken into account in chemical categories, *i.e.*, cci and cii morphisms, where "c" denotes the preservation of the values corresponding to respective operations and "i" means that the values are non-decreasing. For example, the equality $\lambda x = (\lambda')fx$ holds in cci categories, where f is a cci-morphism preserving the atomic number operation values (as shown) and additionally, saving the bonding force values. Besides, it does not cause decreases in the bonding operation evaluations. An example of such assignment has been pictured below in Figure 6.

Finally, all paths leading to distinguishing chemical atoms have been prepared in a purely mathematical way. When the underlying set of a SAC-space (A, λ, ν, \cdot) has only one element, *i.e.*, $A = \{x\}$, then the operations λ , ν , and \cdot are denoted as $\lambda^{x,L}$, $\nu^{x,n}$, and $\cdot^{x,m}$, where L , n , m are the unique values of these functions. Taking into account that the values of the atomic number operation λ depend on a fixed function Λ (*i.e.*, $\lambda \subseteq \Lambda^9$), the atomic chemical forms have been distinguished under general assumptions listed in Appendix II. The results contains Table 2. Let some particular atomic spaces be fixed in the context of correspondence pictured in the diagram of Figure 1. A neutron can be distinguished amongst molecules.

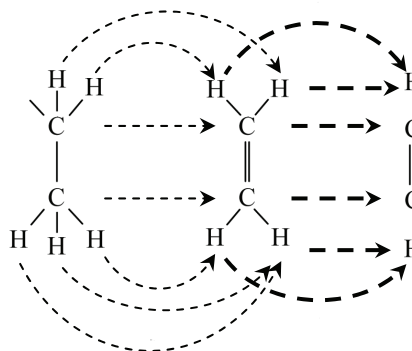


Figure 6. Assignments by cci morphisms between SAC spaces of ethyl, ethylene and acetylene.

Table 1. A classification of self-assembly chemical spaces

SAC space	Saturated	Unsaturated
Connected (non-connected excluded)	Molecules (Mol) <i>e.g.</i> , ethylene or acetylene of Figure 6	Infra-molecules (IMol) <i>e.g.</i> , ethyl of Figure 6
Non-connected and connected included	Molecular spaces (Msp), <i>e.g.</i> , ethylene with acetylene of Figure 6	Infra-molecular spaces (IMsp) <i>e.g.</i> , ethyl with acetylene of Figure 6



In the category of infra-molecules, an electron and proton emerge.



Thus, purely mathematical explorations have revealed the ability of eliciting atomic forms corresponding to empirical findings. This does give rise to pay attention to a theoretical outlook in the search of physically existing species, counterparts of which appear mathematically in Table 2 along with the forms of the basic chemical elementary particles.

DISCUSSION AND CONCLUSIONS

Forms and Polarized Viewpoints on the Role of Mathematics in Natural Sciences

A way leading from mathematics to chemistry is assumed in this work and therefore, the priority has been given to mathematical terms. Inevitable, interdisciplinary crossing analogies (*e.g.*, in terminology or denotations) encountered should not be directly substituted by common, specific to chemistry or physics conceiving. Rather correspondences suggested by the scheme of Figure 1 are to be looked for.

A molecule as a profound discovery of modern chemistry is, in principle, an invention of certain forms in spite of "dressing" them with various concepts of bonding. Contemporary chemistry has been released from alchemy, started and dynamically progressed as a molecular science before an involvement of electronic and quantum theories. For various reasons, the purely chemical notion of a molecule has not been fully incor-

porated in surrounding disciplines. Thence, this is often disguised and implicitly used though results cannot contradict the rules of empirical chemistry.

This is a crucial point to keep a reasonable balance between theory of forms and other contributions, *e.g.*, of quantum theories. Molecular forms can be investigated by robust mathematical means of the graph theory.¹⁰ Since graphs are well grounded in mathematics and they can be carriers of the resultant information on physically existing molecules, their significant role in joining mathematics and chemistry is entirely justified.

One of the features of the current work is approaching self-assembly and coordination compounds as forms subject to a unified viewpoint expressed by "*ab ovo*" determined mathematical properties (*cf.*, Appendix II). Due to the aforementioned idea of mathematically defined saturation, the forms in question can be regarded as a result of specific constraints. For example, for two atomic species of carbon and four of hydrogen, there exists exactly one saturated form $\text{CH}_2=\text{CH}_2$ of ethylene. Such a result of saturations is a rule for primary self-assembly though constraining leads to more than one solution as usual. Coordination compounds owe their forms to the phenomenon of saturation as well. An idea of Alfred Werner¹¹ has led from primary stage of constitution of saturated compounds to the secondary one by a simple concept of "cutting" collections of molecules in the way prompted by experiments and theories of his times. Let the example of Zeise's salt (*i.e.*, potassium (η^2 -ethylene)trichloroplatinate(II), $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$) form be taken into account. A starting collection of primary stage molecular forms consists of saturated species KCl , PtCl_2 , and ethylene. A part of the species involved can mathematically be distinguished (Figure 7) and then transformed into a coordination entity like w of Figure 5. Such experimen-

Table 2. Mathematical forms of chemical atomic species

Space		Morphism	
		<i>cci</i>	<i>cii</i>
Mol	Fe	Empty space	Empty space
	At	?	$\{(\{x\}, \lambda^{x,L}, v^{x,0}, \cdot^{x,0})\}_{x,L}$ for $(x, L) \in \Lambda$
Msp	Fe	Empty space	Empty space
	At	\emptyset	\emptyset
Imol	Fe	\emptyset	\emptyset
	At	$\{(\{x\}, \lambda^{x,L}, v^{x,n}, \cdot^{x,0})\}_{x,L,n}$ for $((x, L), n) \in \Lambda \times \mathbb{N}^*$	$\{(\{x\}, \lambda^{x,L}, v^{x,1}, \cdot^{x,0})\}_{x,L}$ for $(x, L) \in \Lambda$
Imsp	Fe	\emptyset	\emptyset
	At	\emptyset	\emptyset

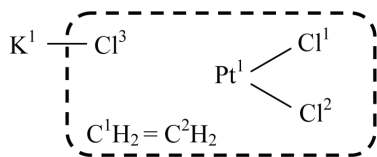


Figure 7. Distinguishing coordination complex form from symmetrized component SAC spaces.

tal and theoretical procedures are commonly pursued by chemists though empirical thinking using experimental results and iconic languages is quite different from the operations performed in mathematical terms in which only sets and rules of operations on them are employed.

Since Cl^3 does acquire an unsaturation (in the mathematical sense (55)), its value is conveyed on the distinguished coordination sphere after removing the relationship between K^1 and Cl^3 . Consequently, the whole coordination species becomes imbued.

$$\begin{aligned} \text{usat}Cl^3 &= vCl^3 - \text{gra}\partial Cl^3 = 1 \\ &= v\omega = \text{gra}\partial\omega \end{aligned} \quad (61)$$

It has already been indicated in the previous section that just considered relationship does not determine the unsaturation in the sense of multiple correspondences between atomic species. Inorganic chemistry knows yet another notion of saturation-unsaturation based on the 18-electron rule count of ligands and central atoms (*cf.*, Ref. 12, p. 817, 822). There is no direct relevance of these notions with the formal conceiving pursued herein and expressed, *e.g.*, by formula (61).

Physico-chemical way of distinguishing analogous to the one outlined in Figure 7 involves a calculation of oxidation and coordination numbers, employing electronic structure or ligand and crystal fields knowledge on interactions between the species involved.⁸ Consider an example of iconic language presentation of empirical chemistry.

Three chlorine ligands and ethylene are at the vertices of a virtual square inserted in the model. The whole coordination sphere is provided with the sign "—" in view of the negative charge of this species. Normally, chemists add information on interactions between central atom (platinum in the case) and ligands by a line, which marks a kind of bonding. Especially peculiar is the so-called dihapto binding with the π -electronic system of ethylene. The information on this is expressed by prefix " η^2 " contained in the systematic name of the compound considered. There is a broad spectrum of concepts in understanding the term "bond" in modern chemistry. In graph based theories and in SAC spaces, connecting lines or arrows have an independent mathematical meaning, which does not need any physico-chemical substitutions. For the structures in question,

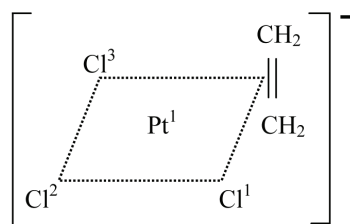


Figure 8. Chemical ideogram of the coordination sphere of Zeise's salt (potassium (η^2 -ethelene)trichloroplatinate (II)).

mathematical sense is free of geometric distances and angles and any electronic or quantum theory entries, though it can be referred to them. Owing to this fact, a theoretician can progress in a purely mathematical manner contrary to the iconic language means of empirical chemistry. Mathematical approach is able to decipher and enrich the information on sophisticated features underlying chemical phenomena by clear eliciting relevancies with derived formal properties. Results obtained by means of certain functions on graphs called topological indices^{10,14} are examples revealing efficiency of the abstract approaches employed.

Is it really so that relationships pictured in Figure 5 would not necessarily be chemical bonds responsible for the molecular geometry? It turns out an equivalent structure does exist.⁹ The information inherent in the previous case implies a correspondence called *involutory injection* (*cf.*, Figure 9). In spite of so radical "extraction" of the chemical information stored in iconic ideograms, sophisticated formal properties unattainable beyond the mathematical treatment can ground and predict experimental results very precisely.¹⁵

The nature of self-assemblage forms is mathematical and they take an essential, though sometimes implicit part of reasoning in empirical chemistry. Syntheses of new compounds inevitably include a design of pure self-assemblage molecular forms in spite of superimposed electronic conditions, steric factors or quantum chemistry premises. Great discoveries like Buckminster fullerenes¹⁶ are due to the anticipating ideas of this kind, though the geometric factor has also contributed this case.

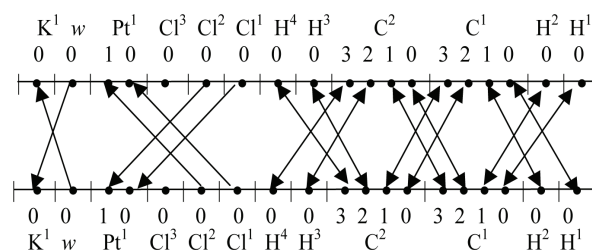


Figure 9. Involutory injection (chemical involution after symmetrization) of Zeise's salt.

Broad information and generic discussion on mathematics and chemistry interfaces can be found in Ref. 1. A few remarks have been added here in the context of the idea of exploration of mathematics in the search for counterparts (patterns) of empirically existing objects and processes.

(i) One pole of opinions claims that mathematics uses the results of measurements to describe the physico-chemical reality in terms of real or complex numbers and their transformations. Mathematical usage of them leads, however, to the empty deliberations from the empirical chemistry viewpoint since no essential progress can be reached due to the mathematical abstract ideas. Simply, this is useless to progress experimental discoveries, *e.g.*, in organic chemistry syntheses. Mathematics is developed as a consideration of consequences of tautologically generated systems of axioms. In principle, a machine could do the same or better than a man. Viennese Circle (Carnap), Popper, Lakatos can be mentioned as representatives of the anti-metaphysical direction in the philosophy of mathematics supporting the concepts just outlined. A concise summary of their views is presented, *e.g.*, in Ref. 17.

(ii) Another kind of opinions on the role of mathematics in the investigations of physical world leads to the modern mathematical realism represented, *e.g.*, by Kurt Goedel¹⁸ or Roger Penrose.¹⁹ This way assumes that mathematical objects and properties are discovered as specific entities accessible to the human mind and therefore the mathematics can yield the same results when approached by many people. The first way, where the products of mathematics are man made, opposes this thesis. For example, sets, relationships, theorems are the same for many mathematicians due to the biological kinship of human beings.²⁰

Considering the status of the objects encountered in mathematics means also to consider the status of patterns for the physical world. Independently of the dispute, which party is right, the correspondence of Figure 1 is difficult to question even if the researcher's position is agnostic or neutral.²¹ Simply, the relationship indicated must be recognized as a fact admitting recognition of nature by mathematical means. They can be treated as tools (*e.g.*, in measurement procedures) or a source of information (patterns). Rejecting this leads to the negation of results of mathematical natural sciences. Besides, it is assumed herein that cognitions through mathematical formalisms and physico-chemical experiments are quite different ways in deciphering properties of the physical world.

If the natural phenomena are describable in mathematical terms, then respective mathematical objects should also support their properties. In this sense, the

developments of mathematics cannot consist only of formal pragmatically oriented manipulations. In order to reach an essential progress, the one must recognize appropriate structures and mathematical properties for particular areas of research. An attitude that all mathematical results are of empirical significance or the recognized mathematics can exhaust all the applied aspects would be naive. There is no, as usual, ready mathematics for the empirical problems. Thence, the modern mathematical physics and chemistry cannot take only the position of a user of mathematics but also inspirations and concrete contributions should be made from these domains of natural sciences.

Chemical recognition of the nature of the structure of matter reveals itself as very resistant, in comparison with other domains of science including physics. Despite the apparent simplicity assessed in the context of modern knowledge, the essential progress in chemistry, especially in theoretical chemistry was relatively very slow during centuries and it remains so. There is a gap of around two thousand years between the first concepts of atoms (Democritus, Epikur, Leukippos)²² and the ideas of R. J. Boscovich inspired by a discussion with Leibniz, which have led to the concepts of forces interacting between atoms. Chemical discovery of atomic and molecular organization of matter dated from Dalton's and Kekule's (*cf.* Ref. 1) time started the immense progress in chemical syntheses and recognition of molecular structure properties. Nevertheless, this progress has never reached the level of contribution, *e.g.*, of mathematical physics in its domain. Thinking in terms of molecules is still an autonomous area of experimentally working chemists having their own, non-mathematical tools in syntheses of novel compounds. One of the reasons is likely due to the fact that chemistry is focused on the resulting properties determining functionality and ability of atomic species to create molecules, while physics is more insisting on internal structural features of atoms.

In this work, some non-standard approach has been examined in testing the ability of mathematical ways to come to the counterparts of the physically existing particles which take part in the creation of molecular structures. A rigorous approach assumes that derivations are based on a system of axioms (Appendix II). Chemical names employed for abstractly determined operations are mathematical conventions reflecting tendencies related to the chemical reality only in a general sense. This formal way has shown certain non-standard solutions as indicated in Table 2. Taking into consideration that a molecular structure turns out to be a symmetry form based on chemical involutions,⁹ a hypothesis on the non-standard compounds has been framed.²³ By the result on atomic species of Table 2, the idea of quite

novel self-organization symmetries acquires additional premises in favor of it. Besides, the modern physics of elementary particles is one of the most fascinating areas of modern science. The concepts and experiments on antimatter particles²⁴ raises a question about hybrid or fully antimatter molecules. To summarize in a few conclusions:

(i) The algorithms of pure mathematics have shown an applicable efficiency in yielding objects that can be interpreted as elementary particles in chemistry.

(ii) The atomic structures derived afford theoretical suggestions and premises to construct non-standard self-assembly symmetries that can support quite novel physico-chemical properties and processes.²³

APPENDIX I

A cognitive scientific interest in number foundations¹ can lead to the recognition of basic mathematical background underlying derivations of abstract atomic species. An entry outline using categories has been shown below. The standard definition of a category can be found, e.g., in Ref. 2. Equivalently, as a generalized group, a category is a multiplicative system (A, \cdot) where, in general, the multiplication is not necessarily determined for all pairs (y, x) of $A \times A$.

$$\cdot : A \times A \rightarrow A$$

If pair (y, x) belongs to the domain of such a *partial* multiplication, then $y \cdot x$ is determined and it is said that such a product does exist. Additionally for a category, the following conditions should be fulfilled:

i) For each element $x \in A$, there is such neutral element a (called an object) that $x \cdot a$ exists and there is such neutral element (object) b that $b \cdot x$ does exist.

ii) For each x, y, z of A , $[(z \cdot (y \cdot x))$ does exist or $(z \cdot y) \cdot x$ exists] if and only if $((y \cdot x)$ and $(z \cdot y)$ exist and $z \cdot (y \cdot x) = (z \cdot y) \cdot x$]

The definition just mentioned shows more clearly a uniformity with algebraic structures used for distinguishing atoms in the previous section.

It is well seen that objects of categories play the role of neutral elements like the unit in a group or monoid. Certain mappings relating categories can be treated similarly as homomorphisms of groups, i.e., they should save multiplication, when determined, and additionally, transform objects of one category into objects of another one. Such mappings are said to be *covariant functors* (briefly called functors herein). Category \mathcal{C} is called concrete provided that there exists a functor f into the category of sets such that each restriction $f|_{\mathcal{C}(a, b)}$ is injective.

Categories, in which one of the most basic properties of natural numbers (with 0), i.e. the principle of induction is encoded, are certain categories with an induction object a^0 . This is a spectacular feature of the fundamental number constructs that by inserting such an object in a category defined below (for short, called conventionally "extensively concrete" one), all objects of such a category acquire properties inherent in the principle of induction. Objects of this kind have been shown by the cases pictured in Figures 2–4. A concrete category is extensively concrete iff the following conditions hold. First,

$$\text{iso}\mathcal{C} \cap f^{-1}(\text{obj}\mathcal{C}_{ns}) \subseteq \text{obj}\mathcal{C}$$

Moreover, for each arrow $x \in \text{iso}\mathcal{C}_{ns}$ and $a \in \text{obj}\mathcal{C}$, if the domain of x equals fa , then there exists such object $a' \in \text{obj}\mathcal{C}$ that

$$x \in f([\mathcal{C}(a, a') \cap \text{iso}\mathcal{C}])$$

The above assumptions are not very strong because any category with commonly structured objects is extensively concrete and practically the whole variety of mathematical structures does support these properties.

In an extensively concrete category X , f (where f is a functor), the object a^0 is said to be an *induction* one provided that:

i) a^0 is initial,

ii) each arrow beginning at a^0 is quotient,

iii) a^0 – equivalences (congruences) are such equivalence relations on \mathbf{N} (\mathbf{N} denotes the von Neumann's natural numbers) that if $m(r)n$, then pair $(m \cup \{m\}, n \cup \{n\})$ fulfils the relation r as well.

Let the terms of the above definition be explained. Object a^0 of a category \mathcal{C} is called initial provided that for each \mathcal{C} -object a , there exists exactly one arrow such that a^0 is its domain and a is its codomain. If \mathcal{C}, f is a concrete category, then the \mathcal{C} -surjection $x: a \rightarrow b$ is quotient iff for each arrow $v: fb \rightarrow i$ and each \mathcal{C} -arrow $y: a \rightarrow e$ such that $fy = v \cdot fx$, there exists such \mathcal{C} -arrow $z: b \rightarrow e$ that $fz = v$. For \mathcal{C} -object a , evaluation results in an object of the category of sets, i.e., $fa = (A, I_A, A)$. *a-equivalences (congruences)* are such equivalence relations on A that canonical surjection $(A/r, s, A)$ is an image of a quotient arrow with the domain a .

As to the induction objects, the following theorem has been proved.

Theorem 1.

Extensively concrete categories with induction objects are counterparts (owing to an isomorphism) of categories arising by means of the principle of induction expressed by the condition (48).

Observe by an immediate corollary that only three types of objects corresponding to the ones pictured in Figures 2–4 exist in categories with an induction object.

An inversion of the relation (51) applied to the categories in question distinguishes atoms corresponding to the Galois' fields and prime numbers. Systems (A, o, S) fulfilling the principle of induction are called induction algebras.^{25,26} They supply a particular example of atom selections for sets with structures. In virtue of Theorem 1, categories with induction objects involving other structures save the "prescription" (51) the same. Thus, its potential in enrichment of patterns for distinguishing atoms in categories based on other species of structure has been elucidated.

APPENDIX II⁵

Axioms are logical statements characterizing mathematical structure. For example, multiplication in object (A, \cdot) can be endowed with the axioms of a group or category. Objects of the form (A, o, S) with a fixed point o and successor S constitute natural numbers, if certain postulates called Peano's axioms³ are satisfied. If none or only a part of Peano's axioms (*e.g.*, only the axiom of induction) is fulfilled, then such, so to speak a pre-object, can also be investigated and interesting properties found. For example, the principle of induction alone also implies *modulo* counting of natural numbers as illustrated in Figs 2–4. In order to obtain only properties of natural numbers applied in common practice of human beings, all axioms in question should be employed. Similarly, if an aptness is inherent in a system of statements characterizing structures in objects like the ones just mentioned, then a range of consequences can formally be derived. It is supposed that an aptness of axiomatically based mathematical systems aimed to concrete applications in natural phenomena is responsible for the efficiency of formal derivations in revealing the needed information encoded in the structure of matter. An axiomatic system⁵ has been distinguished for testing various aspects of applicability in chemistry. The one employed for atomic species selection and for other goals (*cf.*, *e.g.*, Ref. 15) is presented below and it has been formed under guiding idea of saturation, as mentioned above. Chemical names of mathematically determined operations, relations, properties, etc., are conventional and cannot automatically be related to any standard chemical imagination.

A chemistry pre-object is such a system (A, λ, ν, \cdot) that λ (the "atomic number" operation) maps A into the set of natural numbers \mathbb{N} , ν (the "bonding force" operation) is a partial mapping with the domain ($\text{dom}\nu$) included in the set of all subsets of A (denoted $\text{Pow}A$)

into \mathbb{N} , and \cdot (the "bonding" operation) is a partial mapping from the Cartesian product of subsets of A ($\text{Pow}A \times \text{Pow}A$) into \mathbb{N} .

To obtain commutative bonding operation, a symmetrized multiplication is useful:

$$u \cdot w =: \max\{u \cdot w, w \cdot u\}$$

The non-zero values of the bonding operation yield the following relationship:

$$r =: \{ (u, w) \in \text{dom}\cdot \mid u \cdot w \neq 0 \}$$

There are several groups of axioms which correspond to the operations mentioned or to the pairs of them.

(i) Axioms for the underlying set A

U₁ - This group includes only one axiom in which finiteness of the set A is postulated, *i.e.*, A has cardinality $n \in \mathbb{N}$.

(ii) Axioms on the operation λ with values called atomic numbers

AN₁ - The condition of the fixed atomic numbers. This statement assumes the inclusion of the atomic number operation λ in a general function Λ . Formally,

$$\lambda \subseteq \Lambda$$

Function Λ has been defined on the Grothendieck universes^{9,27} and adopted to the chemical goals.

(iii) Axioms of the "bonding force" operation

BF₁ - The condition of the empty set. The exclusion of the null set from the domain of bonding force operation is asserted. In symbols,

$$\emptyset \notin \text{dom}\nu$$

BF₂ - The condition of one element classes. In virtue of this axiom, the one element subsets of A (denoted A/I_A) are included into domain of the "bonding force" operation. Formally,

$$A/I_A \subseteq \text{dom}\nu$$

BF₃ - The condition of separation. Due to this statement, the multi-element classes of the domain of the operation ν are separated. Symbolically,

$$\forall u, w \in \text{dom}\nu \setminus A/I_A : u \cap w \neq \emptyset \Rightarrow u = w$$

A consequence implied by this axiom is such that multi-element sets of $\text{dom}\nu$ are maximal, *i.e.*, for each $u \in \text{dom}\nu \setminus A/I_A$ there exist no neighborhoods of u different from u .

(iv) Axioms for the "bonding" operation

B₁ - The condition of the excluded inclusion postulates

the null values of the bonding operation for such pairs of subsets of A which are related by inclusion. Formally,

$$\cdot \quad r \cap (\subseteq_{\text{Pow}A} \cup (\subseteq_{\text{Pow}A})^{-1}) = \emptyset,$$

where $\subseteq_{\text{Pow}A}$ denotes the relation of inclusion in $\text{Pow}A$.

B₂ - The condition of the one direction of a bonding relationship. This statement establishes that if $u \cdot v$ and $v \cdot u$ are different, then one of the values equals 0. In symbols,

$$\begin{aligned} \cdot \quad \forall (u, v) \in \text{dom} \cdot : (u \cdot w \neq w \cdot u) \Rightarrow \\ (u \cdot w = 0 \vee w \cdot u = 0) \end{aligned}$$

(v) Axioms for pairs of operations

BO₁ - The condition of the domain of bonding operation. Due to it, the domain of multiplication includes only pairs from the domain of bonding force operation. Formally,

$$\text{dom} \cdot = \text{dom}v \times \text{dom}v$$

BO₂ - The condition of the resultant bonding force operation. The null value of v for multi-element classes is postulated if all the classes properly included are saturated. Symbolically,

$$\forall u \in \text{dom}v \setminus A / I_A : ((\forall w \in \text{dom}v, w \subset u : vw = \text{grad}w) \Rightarrow vu = 0)$$

For $w \in \text{dom}v$,

$$\text{grad}w =: \sum_{w' \in d}^S w \cdot w', \text{ where}$$

$$d =: \text{dom} \cdot (\{w\}).$$

Since the axiom **BO₁** implies equality $\text{dom} \cdot = \text{dom}v \times \text{dom}v$, $d = \text{dom}v$ after usage of **BO₁**. Thence, a less general expression (53) becomes a consequence of **BO₁** and more general definition of grades just introduced.

SAT₁ - This axiom of saturation claims that the grades are bounded above by bonding force values, *i.e.*,

$$\forall u \in \text{dom}v : \text{grad}u \leq vu$$

Z₁ - The condition of zero atomic number classes. There are only restricted relationships distinguished between forms with zero atomic number values and any others. Thus, non-chemical, *i.e.* particularly belonging to the physics of elementary particles "bonding" relationships are eliminated. Formally,

$$\forall (u, w) \in r : \neg u \subseteq \lambda^{-1}(\{0\}) \ \& \ \neg w \subseteq \lambda^{-1}(\{0\})$$

This axiom discriminates r - relationships for as-

semblies which include null atomic number elements only. In chemical terms, the statement **Z₁** claims that only protonated species can constitute non-atomic molecular or infra-molecular forms.

Self-assembly chemical (SAC) spaces are determined by the axioms listed above.

Additional axioms

Certain additional conditions specific to the forms listed in Table 2 have been introduced for a better precision in derivations of atomic species. These are the following.

B₃ - The axiom of connectivity. Observe that the domain of bonding operation $\text{dom} \cdot$ is a relation distinguishing such pairs of subsets of A , which can be multiplied. Therefore, the domain of this relation (*i.e.*, $\text{dom} \cdot$) selects elements which are admitted to be multiplied by subsets in question. This is easily seen that due to the axiom **BO₁**, $\text{dom} \cdot = \text{dom}v$. The postulate of connectivity does express a condition in virtue of which any two different elements (u, w) capable to be related by bonding operation and not embraced by species different from them, are fulfilling the relation

$$\cdot \quad (r)^n$$

The latter one is the n -th composition of the symmetrized relationships (57). In symbols,

$$\forall (u, w) \in (\text{dom} \cdot)^2 : (u \neq w \ \& \ \text{Nb}(u, (\text{dom} \cdot) \setminus \{u\}) = \emptyset =$$

$$\text{Nb}(w, (\text{dom} \cdot) \setminus \{w\})) \Rightarrow$$

$$\exists n \in \mathbb{N} : (u, w) \in (r)^n$$

SAT₂ - The strong axiom of saturation. It can be applied for both stages of molecular constitution provided that the species involved are maximal.

$$\forall u \in \text{dom}v : \text{Nb}(u, \text{dom}v \setminus \{u\}) = \emptyset \Rightarrow \text{grad}u = vu$$

If the domain of bonding force operation $\text{dom}v$ consists only of one-element sets, then for any $u \in \text{dom}v$, there are no proper neighbourhoods of it, *i.e.*, $\text{Nb}(u, \text{dom}v \setminus \{u\}) = \emptyset$ and thus, condition **SAT₂** implies the axiom of saturation for the primary stage of self-assembly.

$$\forall u \in \text{dom}v : \text{grad}u = vu.$$

BO₃ - The strong axiom of the resultant bonding force value. Coordination entities have chemically associated certain resultant number depending on the saturation of central atom or atoms under their oxidation number. Following this idea (Werner – 1893), a weak condition

Table 1'. Formal complements to classification of self-assemblage chemical spaces of Table 1

<i>SAC space</i>	<i>Saturated</i>	<i>Unsaturated</i>
Connected (non-connected excluded)	Molecules (Mol) SAC spaces & B ₃ & SAT ₂ & BO ₃	Infra-molecules (IMol) SAC spaces & B ₃ & –SAT ₂ & BO ₃
Non-connected and connected included	Molecular spaces (Msp) SAC spaces & SAT ₂ & BO ₃	Infra-molecular spaces (IMsp) SAC spaces & –SAT ₂ & BO ₃

BO₂ has been introduced. A stronger one, exactly determining the induced bonding force value, is of the following form:

$$\forall u \in \text{dom}v \setminus A/I_A: vu = \sum_{w \subset \text{dom}v} (vw - \text{gra}dw)$$

Finally, after determination of the mathematical background, Table 1 can be completed by respective logical statements precisely determining mathematical sense of the notions employed in derivations of atomic forms. Thus, each molecule is a molecular space and each infra-molecule is an infra-molecular space. The opposite relationship does not hold.

The axioms listed above become especially simple when each element of the domain of bonding force operation is a singleton, *i.e.*, $\text{dom}v = A/I_A$. If such particular property holds, then postulates of Table 1' are sufficient to prove atomic forms of Table 2. If however, multi-element classes are involved, then proving atomic molecule (Mol) and infra-molecule (IMol) forms of Table 2 needs a natural assumption that there exist at least two species of $\text{dom}v$ with non-zero value of their product. Formally,

$$\text{dom}v \setminus A/I_A \neq \emptyset \Rightarrow r \neq \emptyset$$

Bounding above grades of elements of the bonding force operation expressed in axiom SAT₁ discriminates over-saturated structures. They fall in the scope of the so-called supra-molecular chemistry. Specific forms emerging in this domain are attributed by inequality

$$vu < \text{gra}du,$$

for certain u of the domain of bonding force operation. Such structures would satisfy the axioms of SAC spaces with excluded condition SAT₁. Transformations into involutory injections (like in Figure 9) can also be performed by an extension of the bonding force operation, *i.e.*,

$$v'u = vu + \varepsilon$$

and thus receiving the effect similar to the condition of SAT₁, *i.e.*,

$$\text{gra}du \leq v'u$$

Primary and secondary stages of molecular self-assemblage are well empirically established as the result of saturation-unsaturation phenomena. This is not so in the case of strongly hypothetical relationships distinguished in supra-molecular chemistry. A glance on mathematical modifications of axioms beyond the condition SAT₁ is given here to signal a mathematical way only. Forms proper for higher stage of molecular self-assembling can be quite different from the ones aforesaid. For example, objects of the category of labeled sequences^{28,29} are more practical and efficient in the essential part of biochemistry than a direct usage of SAC-spaces.

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SAŽETAK

Matematički uzorci u kemiji – na prekretnici stvaranja simetrije molekularnog samosastavljanja

Lech P. Schulz

Department of Chemistry, Adam Mickiewicz University, Poznan, Poland

Pružaju li abstraktna matematika obrasce za kemiju? Podrazumijeva se da matematika ima svoje, autonomne kriterije razvoja i da matematička kreativnost ne može napredovati jednostavnim "slijepim" nabranjem mogućih tautologija. Istovremeno, primjenjena dostignuća u neovisno razvijanim područjima matematike su prilično rijetki slučajevi. U ovom je radu pokazano da su naizgled abstraktni, i pretpostavljeno bez izravne primjene koncepti čiste matematike, doveli do konkretnih entiteta koji se susreću u kemiji. Zbog svega toga su uvedene opće definicije molekularnih oblika i matematičkih atoma kako bi se dobili objekti koji odgovaraju temeljnim česticama u kemiji. Osim toga, korištenje obrazaca temeljne aritmetike, dovelo je do posebnih relacija za određivanje takvih atomskih vrsta u određenim kemijskim kategorijama. Naglašeni su aritmetički temelji kemije, a nagoviještene su i moguće nadogradnje.