

Varieties of *Chemical* Closure:

Three Kinds of Coherence Observed in Chemical Systems, and Their Relation to Societal Integrations

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ABSTRACT

Covalent bonding within chemical molecules and the internal electronic structure of atoms involve closure of phase relations of electronic wave functions, as suggested de Broglie by many years ago. The structures of crystals involving positive and negative ions can be understood in terms of replication of unit cells that may be classified in terms of symmetry. The main principle involved in crystal symmetry can be understood through examination of possible patterns in decorative borders. A more widely applicable type of chemical closure occurs in oscillating reactions (dissipative structures), in which an autocatalytic process is balanced by some exit reaction. As is the case for the other types of chemical coherence, the number of distinct types of oscillating reaction is rather small. Otherwise puzzling aspects of human social and organizational behavior may be clarified by analogy with chemical oscillating reactions.

INTRODUCTION

Chemistry deals with the world on many levels. Major industrial chemicals are produced in truly mind-boggling quantities. Chemists also deal with unimaginably *small* magnitudes. Chemists can now see and manipulate *single* atoms, molecules, electrons, protons – all sub-sub-microscopic entities. On these levels and the many intermediate ones, *closure* is critical. *Symmetry* – the property of being unaffected by some possible change – is intimately tied up with chemical

closures of all sorts. This paper considers *closure* at several chemically-relevant levels, and suggests that considerations similar to those used in chemistry might usefully be applied to questions of wider interest.

ELECTRONIC CLOSURE

Nineteenth century chemists described the properties of the elements of the periodic table, including each element's tendencies to produce compounds of various formulas, and also studied the colors that each element imparted to flames (yellow for sodium, green for boron, etc). By the turn of the century, organic chemists had deduced that the four bonds to carbon in many hydrocarbons were directed in specific spatial directions – toward the vertices of a tetrahedron. Inorganic chemists then inferred that the six bonds of certain cobalt complex compounds were pointing toward the corners of an octahedron. Early in this century, G. N. Lewis used all this specifically chemical information in devising his electron-octet theory of bonding between atoms. N. Bohr added considerations from detailed study of black-body radiation and flame spectra and expanded these ideas into his theory of the electronic structure of the atom. Bohr's initial approach considered the maximum number of electrons in the several electron-shells of the atom as free parameters with no justification other than the pragmatic one that those few numbers rationalized the periodic nature of the chemical and physical properties of the elements to a significant extent. The key to a deeper understanding was provided by Prince Louis de Broglie's fanciful suggestion that the electrons in atoms somehow had *wave properties*, so that the only permissible size of the electron's orbit around the atomic nucleus is one in which the length of the path around the orbit (two π times the radius for a circular track) was equal to a whole number of wavelengths (λ , lambda) of the electron-wave. Clearly, the de Broglie formula, $2\pi R = n \lambda$, describes a type of closure that is highly significant in chemistry. When combined with the *Pauli exclusion principle* – no two fermions (electrons) in a system can be in exactly the same state – de Broglie's simple postulate brings the rough outline of the quantum concept of reality into view. This sort of coherence is basic to all theoretical understanding of chemical bonding.

The original insight of de Broglie has been developed and elaborated in great detail. Rather than considering a one-dimensional electron-wave wrapping around an atomic nucleus, nowadays we describe the condition (probability density) of electrons in atoms in terms of "wave functions" and "spherical harmonics" – three-dimensional shapes (usually called "orbitals") with various numbers of nodes – but the principle is quite the same. Related considerations also apply to electrons in molecules of all sorts. "Molecular orbitals" are quantized (exist only in integral steps)

just as de Broglie's electron-waves were, and for the same reasons – closure of phase relations of electron wave functions is required for persistence.

Stability in molecular structure always involves a delicate balance of attractive forces (arising from unlike electrical charges) and repulsive interactions (from like electrical charges, Pauli exclusion). When electrons get to spread out over several atoms, negative-negative repulsion is decreased. For this reason more symmetrical arrangements of atoms are more stable than corresponding but less symmetric structures.

SPATIAL CLOSURE

Minerals and other inorganic crystals display a wide range of complex structures and provide interesting examples of the importance of closure in chemistry, but that field is too complex for this short paper. The main point of symmetry and closure in crystals can be illustrated by types of borders found in decorative art-work – from medieval manuscripts through oriental carpets and to Hungarian needlepoint.¹ Each such border consists of a unit that is repeated as often as necessary to complete the circuit around the surface to be decorated.

- 1.) P P P P P P P P
- 2.) C C C C C C C C
 C C C C C C C C
- 3.) Z Z Z Z Z Z Z Z
- 4.) V V V V V V V V V V
- 5.) C C C C C C C C C C
- 6.) O O O O O O O O O O
 O O O O O O O O
- 7.) X X X X X X X X

Figure 1. The seven symmetry classes of one-sided bands. (See text.)

All borders can be divided into seven (only seven) symmetry classes, according to whether the repeating pattern would be unchanged under specific possible operations. (Recall that

symmetry is immunity to a possible change.) We can illustrate these abstract pattern-classes using letter symbols (Figure 1). (Please ignore features such as the barb on C.) The **first** class of pattern is unchanged by sliding to the right or left one unit (closure here), but under no other operation. (All the classes are symmetric under such *translation*.) The **second** class is unchanged by the operation of sliding one half unit to right or left and then flipping over the horizontal center-line (part of a "*glide-reflection*" plane) to restore an arrangement indistinguishable from the starting condition – a different type of closure. The **third** class of border is unchanged by a 180-degree rotation around an axis rising *perpendicularly* from the midpoint of any letter. The **fourth** type of band is symmetric about a *vertical axis* bisecting any letter. The **fifth** sort of edging is symmetric to a rotation about a *horizontal axis*. The **sixth** class is unchanged by a *glide-reflection*, and also by rotation about a *vertical axis*. The **seventh** pattern-type has the highest symmetry, with *both horizontal and vertical* symmetry axes. (It is left as an exercise for the reader to locate an oriental carpet, and to assign its border to one of these classes.)

Each of these patterns has a different kind of closure. Each pattern has a unit that can be replicated indefinitely so as to fill an endless line. In a similar way, all tile patterns (such as those found in Moorish art in Spain) have a basic unit that fits together with others of its kind to fill every bit of a plane, extending as far as one likes. (It is easy to tile a floor with squares, hexagons or octagons. If someone has sold you a large supply of pentagonal floor tiles, you have a problem – there is no simple pattern involving only pentagons that will fill a plane.) Correspondingly, there is a limited, though large, number of ways that three-dimensional units can fit together to fill space completely. (There are total of 230 three-dimensional space groups.)

During the last twenty years, crystallography has been revolutionized by the discovery of "quasi-crystals" – solids that have long-range order that is almost (but not quite) periodic, and the related Penrose patterns – two-dimensional figures that can tile the plane so that recurrence of a given structure is neither completely regular, as in a crystal, nor completely random, as in a glass or liquid. These are closures too, but of rather complex sets of relationships.

TEMPORAL CLOSURE

Some philosophical systems emphasize the importance of substance – by one definition "the unchanging subject of change." Others² call attention to the ubiquity of "process." The most ancient maxim of Western philosophy is *panta rhei* – "everything flows." The papers in this volume are not much concerned with structures that fill spatial dimensions, but are very much

concerned with structures that *fill time* – arrangements of processes that can persist over extended periods while exchanging materials and energy with their surroundings. These are called "dissipative structures" and are contrasted with "equilibrium structures" such as crystals, that could persist if totally isolated from their surroundings.

Whenever nature involves what seems to be a *constant* concentration of some chemical, close examination leads to the recognition that the concentration really varies, but is maintained near its average value by some sort of oscillatory network of processes. Many technological devices are similar. A home thermostat does not maintain a pre-set temperature steadily, but rather achieves the purpose for which it was designed by small oscillations above and below the pre-set target value. On the basis of the contemporary scientific understanding, we now recognize that entities formerly thought to be substantial and perduring are resultants of *networks of processes*. What sort of relationships between components might give rise to a collection of entities *behaving as a unit*. We consider chemical dissipative structures (oscillating reactions³) as examples of unit-determination. Analogous unit-determining properties (better, unit-determining *closures of sets of relations*) can be seen to occur at other levels – from the quantum level, through the societal level, to the cosmological level.

In order for a chemical dissipative structure (oscillating reaction) to exist, the system must be *far from equilibrium* and there must be no stable steady state accessible to the system. When parameters governing the system change, it sometimes happens that a previously stable stationary state becomes unstable. For instance, at ordinary air temperatures, heat generated by fermentation inside a haystack diffuses out of the pile of dead grass, and a quasi-equilibrium steady state is reached. However, when the ambient air temperature is higher than usual, the rate of exit of chemically generated heat is reduced, and the haystack tends to heat up. Since fermentation occurs more rapidly at higher temperatures, retention of heat causes additional heat to be generated faster and faster. The quasi-equilibrium state becomes unstable. The pile of hay quickly becomes quite hot, and may burst into flame.

The circumstance that increase of temperature causes increase of the release of heat and yet further rise in temperature is a particular example of *autocatalysis*. A chemical reaction produces a product (heat in this case) that *increases* the rate of production of that product. Autocatalytic processes abound in nature. Genes are biological catalysts that make copies of themselves (through complicated means). Nuclear reactions produce neutrons that initiate yet further neutron-releasing nuclear reactions. Human groups socialize their members to engage in behavior

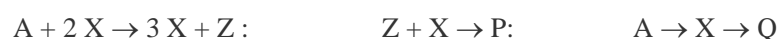
that increases the number of those members. Resources invested in bull markets produce yet further resources to enable additional investments. Each such process can de-stabilize prior steady states – either equilibria or quasi-equilibria.

Every dissipative structure must involve at least one autocatalytic reaction. The simplest kinds of autocatalysis (to which others can be reduced) can be represented:

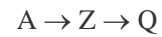
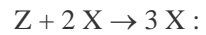


Any autocatalytic process can be the basis of a "clock reaction" – a reaction that is apparently quiescent for a long period of time, and then bursts into activity – a solution changes color rapidly after a time without apparent change, for instance, or a haystack suddenly bursts into flame. A virus (an autocatalytic agent) may lurk undetected for years, then replicate explosively in a short period. The length of the "induction period" is found to depend on the initial concentration of autocatalyst. The rate of production of autocatalyst will initially be low if the starting concentration of the autocatalyst is small. (This accounts for the long time during which not much appears to happen.) But no matter how low that rate may be, the concentration of the autocatalyst continually increases, and the autocatalytic reaction gets faster. This gives rise to an "explosion" of the amount of autocatalyst.

But something else is required to turn an autocatalytic process into a dissipative structure: there has to be some way or "resetting the clock" – of returning the autocatalyst concentration to its initial low value. This requires the existence of at least one additional chemical species. The autocatalyst is usually called X and the "exit species" designated Z. Here are representations of two types of oscillators; both based on cubic autocatalysis, but each using a different strategy to reset the clock. Both of these are *open* systems, with species entering and leaving the system.



In this first case, Z is a byproduct of the autocatalytic process: Z also has the ability to remove the autocatalyst. As the autocatalytic reaction proceeds, the exit species Z builds up, and Z combines with X to remove the autocatalyst from the system. The autocatalyst is fed into the system, and departs from the system (e.g. decomposes). A is the (constant) supply of reagents; P and Q are products that play no other part in the reaction system.

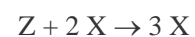
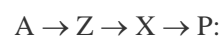


In the second case, Z is not a product, but is a reactant in the autocatalytic reaction. Z is used up in the autocatalytic reaction proceeds. Once Z is depleted, autocatalysis stops. Both the autocatalyst X and the exit species Z are fed into the system and both leave the system by decomposition. In these two simple cases, autocatalysis is controlled by the exit species. In the first case it is choked off by buildup of a toxic byproduct, in the second case the autocatalysis is starved by shortage of a necessary reactant. Any known chemical oscillation that is based on cubic autocatalysis can be shown to correspond to one or the other of these two reaction types.

Oscillations based on quadratic autocatalysis must involve three (or more) variables, usually including a "feedback species," generally called Y. Like reactions based on cubic autocatalysis, these are divided into a few basic categories. It is a remarkable fact that all known chemical oscillators can be divided into a number of categories⁴ that is smaller than the number of symmetry classes of borders discussed above!

Figure 2. Variation of stability of steady states, as pump rate and rate constant for formation of autocatalyst are varied, for the chemical system described in the text.

For simplicity, we confine our attention to a version of the second cubic autocatalytic system shown above, with spontaneous linear (not autocatalytic) formation of X from Z and spontaneous decompositions of X to produce an inactive product.



There are only two variables, X and Z. Important parameters in this system include: proportionality (rate) constants for each of the three chemical reactions, and the pump-rate for the input of Z. For fixed values of the other parameters, we may examine the behavior of the system

as two parameters are varied (Figure 2.). For parameter values that correspond to one region of this two-dimensional space, there is a stable steady state with high autocatalyst concentration. By analogy with the most studied specific reaction of this sort, we call this state "blue". For parameter values corresponding to another region of the diagram, there is a stable (self-restoring after disturbance) steady state with low values of the autocatalyst X concentration – we call this state "red." For parameter values corresponding to a small region of this space, *both* of these steady states are stable. In this region we have a *bistable system*. The color of the solution may be either blue or red, depending on its past history. If this region of parameter space is entered from the blue side, blue will prevail: if it is entered from the red side, red will obtain. There is a third steady state in the bistable system, but it is unstable – any fluctuation will cause the system to move to one or the other of the two stable steady states.

If the parameters correspond to a fourth region of the parameter space, sustained oscillations occur. In this region, both blue and red states are unstable (as is the third steady state, roughly corresponding to the equilibrium state). The system will move repeatedly from something approximating the blue steady state to something approximating the red steady state. In such cases, if one plots the state of the system at various times in a two dimensional space (one dimension for each of the two concentrations), one obtains a *closed* trajectory that goes around the point corresponding to the unstable (third) steady state (Figure 3), rather than a trajectory smoothly approaching the red or blue steady states, which would be obtained with other parameter values. A proper dissipative structure corresponds to a "limit cycle" in some appropriate space. That is, there is a single, closed, curve that describes the sequence of states that the system follows over time. This same single, unique trajectory is eventually attained no matter what the starting conditions might be. In the case that we are discussing, the appropriate space is the [X] - [Z] plane. (As usual, brackets -sometimes omitted- denote concentrations.) We can divide this limit cycle trajectory curve into four segments, using the points at which each of the two variables changes direction of motion (reaches a maximum or minimum) as the points of division.

Figure 3. Trajectory of the state of a pumped autocatalytic chemical system (see text) in the space of concentrations of autocatalyst X and exit species Z , showing a stable limit cycle reached from all starting conditions. This occurs under conditions corresponding to the unshaded region of Figure 2.

In one segment (A), X increases rapidly, while Z decreases. This segment is dominated by the autocatalytic reaction. In a second segment (B), the autocatalyst X begins to decrease while Z also continues to decline. The autocatalytic reaction is now competing with decomposition of the autocatalyst. In the third segment (C), X decreases to a low concentration, and Z increases a great deal. The autocatalytic reaction is now shut off, but decomposition of the autocatalyst is

proceeding, and the feed of Z is significant. In the fourth segment (D), both Z and X increase somewhat. The concentration of X has fallen so low that decomposition of the autocatalyst is not important. As the feed increases the Z concentration, spontaneous non-autocatalytic production of X from Z occurs. When the X concentration passes a critical value, the autocatalytic reaction reaches a high rate, and loss of Z far exceeds the rate at which Z is being fed in, so there is a rapid increase of X and a decrease of Z. As James Joyce would have it, "*Finagin*." The cycle is complete – closure again!

In order for the oscillation to have long-term stability, the trajectory must return to the same condition at which it started. (This is what closure means, in this context.) Compared to the total range of parameter space, the region in which this condition is met may be quite small. But still, this region is large enough that considerable tolerance exists for variation in parameters. (Variation of parameters, within the oscillatory region, gives rise to changes in frequency and amplitude of the oscillation.)

Here, then, are the constraints on origin of a dissipative structure in a chemical system:

- Affinity must be high. (The system must be far from equilibrium and unstable.)
 - There must be an autocatalytic process.
 - A species that can reduce the concentration of the autocatalyst must be available.
 - There must be a *closure* of the network of reactions such that a state sufficiently close to the original condition is achieved.

So long as all these constraints are met, the dissipative structure continues to exist, and can serve as a center of agency. Interactions of the system with the rest of the world are quite different in the presence of the dissipative structure than they would be in the absence of that self-organized coherence. The effects of the structure as whole are the vector sums of the effects of the components, but the concentrations of the components that exist at any instant are the effects of the *closure* of the limit cycle. This is an example of a kind of "downward causation," an influence on the components arising from the thing those components constitute.

The "toy model" used to illustrate the discussion above is nearly the same as the model used to understand the generation of calcium oscillations in biological cells.⁵ These oscillations are known to function in the control of complex biological organs, such as the human brain. (Remarkably, it is the frequency, not the amplitude, of the calcium oscillations that is decoded as

the controlling signal.) The signal is generated by the *closure* of the regulatory network that defines a dissipative structure, and the information transmitted results from subtle alteration in the parameters that control that oscillation. Closure of a dissipative structure increases the rate of entropy generation, compared to an otherwise similar situation absent the dissipative structures. By the sort of downward causation alluded to above, the existence of dissipative structures accounts for the existence of high energy molecular forms, such as sugars, proteins, and DNA molecules. Any understanding of the general direction of evolution must deal explicitly with the sorts of organization discussed in this paper.

SOCIETAL ANALOGIES

The postulate of de Broglie, central to the development of quantum mechanics, is strikingly similar in some respects to the position being advocated above. There are stringent conditions on the closure of sets of relationships. Once that closure is attained, a system maintains its coherence indefinitely, and can function as a unit in yet higher-level coherences. Similar situations, where *closure* of a network of processes has important effects, occur in many fields. Networks of interaction with similar characteristics abound in biochemistry, molecular biology, organismic biology, ecology, sociology, economics, and politics. In favorable cases, systems in all these areas display "unit making" closure of relationships quite similar to those displayed by dissipative structures. This has important consequences of a properly philosophic nature.⁶

William H. Sewell, Jr.⁷, has reconsidered the notion of "structure" in social science:

.....structure, then, should be defined as composed of schemas, which are virtual and resources, which are actual (p13).... a capacity for agency...is inherent in all humans... Just as a linguistic capacity takes the form of becoming a competent speaker of some particular language....agency is formed by a specific range of cultural schemas and resources available in a person's particular social milieu. (p. 20) ...Agency is collective as well as individual (p. 21).

Upper-level relationships (schemas) organize various items (resources, including persons) in such a way that characteristics of the human individuals are strongly influenced, especially as regards modulation of the rate of reproduction⁸. Stability of each social structure is based on autocatalytic population growth, coupled with suitable quasi-automatic regulation.

A particularly interesting example of societal closure is provided by Ostrom, et al.⁹ in an analysis of how human populations evolved means to escape from the "tragedy of the commons." As in the case of the quasi-crystals and Penrose patterns, societal closures occur in ways that are

far from obvious. Modern (science-related) interventions in traditional agricultural practices sometimes destroy preexisting closures and fail to replace them with equally effective substitutes.

Transformations of social structures occur for specific and idiosyncratic historical reasons (fluctuations) but only when stability relationships between structures are favorable. Such transitions involve aspects that can be identified in the systems studied by the more basic sciences, as well as features specific to the upper levels at which the transition occurs. Both in evolutionary biology and in human social functioning, autocatalytic processes combine to yield coherences at many levels – aggregations that themselves have properties, including causal powers. Progress in philosophical understanding of general features of the origin of multilevel coherences seems likely to come from increased attention to how actual, specific, intermediate-level unit-determining syntheses occur. Certain general features of such closures are particularly easy to study at the chemical level.

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