Periodic Systems of Molecules: Physical and Chemical

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Abstract

This paper is a review of research on molecular periodic systems, a developed field of research. The distinguishing characteristics of Physical Periodic Systems are that they include only molecules with a given number of atoms, e.g., diatomic molecules \((N=2)\), and that all relevant molecules with that number of atoms are or can be included. Physical Periodic systems are defined as follows: a Physical Periodic System for \(N\)-atom molecules is the outer \(iV\)-product of an originating atomic periodic table, or can be generated from such a product system by use of slicing or projection techniques to include only molecules with a given number of atoms, e.g., diatomic molecules \((N=2)\); they include recent classifications based on group dynamics. The distinguishing characteristic of Chemical Periodic Systems is that they contain molecules with differing numbers of atoms. It is also a characteristic that they include only molecules stable under a well-known set of conditions (such as atmospheric-pressure wet chemistry). Work related to each kind of system is described chronologically, whether or not the work was identified as a periodic system by its author. All publications claiming to present molecular periodic systems (and of which the authors are aware) are listed, in an effort to achieve a complete review of the rapidly growing field. Finally, a recommendation is made that future classification systems be identified as Physical or Chemical periodic systems, in accordance with the distinguishing characteristics. Care should be taken to ensure that a system truly displays periodicity, and is not just an interesting lattice.
1. Introduction

The periodic chart of the elements is well-known in physics and is the background of modern chemistry. But there has been an extensive development of periodic systems of molecules which is often ignored in chemistry and is even less frequently discussed in physics. The reasons given for this lack of enthusiasm usually include the following:

.. Molecular periodicity follows from atomic periodicity,

.. Ab-initio computations or laboratory experiments are adequate to obtain data for any desired molecule, without reference to a periodic system,

.. The number of molecules is for all practical purposes infinite, and the number of them for which data have been determined is such a small fraction of the whole that the problem of determining global trends is insuperable, and

.. Many molecular structures which can be written on paper do not exist under standard laboratory conditions, so there is little use to place them in a classification scheme.

In spite of these objections, periodic systems of molecules have been a subject of active research (Fig. 1). Many of them fit existing data quite well and have been successful in forecasting new data; some of them have a theoretical basis. Those who participate in this research are optimistic that it will play a more central role in the scientific thinking of the future.

The molecular periodic systems described in this paper were explicitly proposed as molecular periodic systems unless here indicated otherwise (i.e., some very nice systems were not identified as such by their authors). In general terms, they are presented chronologically, in order of first publication, within each section.

2. Periodic charts of the elements

Periodic charts of the elements are not within the scope of this report, but attention is called to several concepts which will reappear later.
Fig. 1. The number of new molecular periodic systems per year, as a function of the year of publication (or, if unpublished, year of communication to the first author). The first, 1862, entry refers to Newlands, J. A. R.: "On the construction of tables exhibiting the composition and mutual relations of organic substances," J. Chem. Soc. (London), 15, 36-40. One of the three entries for 1993 is related to Ref. 75; another is the work described as the final example in Section 3.3; the third arrived so recently that there exists no discussion of it in this paper.
There is at least anecdotal evidence that Mendeleev constructed his chart by writing elements’ names and properties on bits of paper, which he arranged such as to achieve an optimum arrangement. One could just as well imagine that he graphed various properties of atoms on the atomic-number line, and then cut the line such that repetitive portions were placed above and below each other (a "cut and stack" scenario). In any event, the periodic chart can be considered as a two-subscript matrix \( P_{RC} \), where \( R \) denotes the row (period) number and \( C \) denotes the column (group) number. Data for a given element can be approximated by interpolation from data for the adjacent elements along the \( R \) and \( C \) directions and along the diagonal directions (the triad principle).

It is presently considered that the chart is derived from quantum mechanics; in actual fact, this "derivation" consists of collecting computations of atomic properties one atom, or a few atoms, at a time (just as if they were experimental data). On the other hand, group-dynamical methods have proven very capable of deriving the overall structure of the periodic chart.

The placement of the elements in the periodic chart differs if ionized elements are considered. In the extreme case of hydrogen-like ions, each shell is filled in \( n = 1, 2, \ldots \) order, and within each shell the subshells are filled in s, p, d, f order; there exist group-dynamic explanations of this phenomenon.

The symbols at the bottom of Mendeleev’s 1869 chart are important, indicating that much of the data with which Mendeleev structured his chart had to do with the manner in which atoms react with other atoms to form molecules and compounds. Symbols under groups I through VII (\( R_2O, RO, R_2O_3, RO_2, R_2O_5, RO_3, \) and \( R_2O_7 \) (where \( R \) in this context is any element in the column) indicated with how many oxygens the group’s atoms can combine with to make closed-shell molecules (or compounds).

Additional symbols, \( RH_4, RH_3, RH_2, \) and \( RH \), showed with how many hydrogens the atoms of groups IV through VII can combine to make closed-shell molecules; these symbols constitute a portion of the hydrogen-displacement-principle diagram (Fig. 2), which will be mentioned again in Section 4.2.
Fig. 2. Grimm's arrangement of second-row non-metallic atoms and of the pseudoatoms which are formed when they combine, according to the hydrogen displacement law, with various numbers of hydrogen atoms. V is a valence which is 1 for carbon and 4 for neon; H is the number of hydrogen atoms. Used by permission from PERIODIC SYSTEMS AND THEIR RELATION TO THE SYSTEMATIC ANALYSIS OF MOLECULAR DATA, The Edwin Mellen Press, Lewiston, NY (Ref. 5).
3. Physical periodic systems

3.1. Characteristics of physical periodic systems

The distinguishing characteristics of physical periodic systems are that they include only molecules with a given number of atoms, e.g., diatomic molecules \((N=2)\), and that all relevant molecules with that number of atoms are included. Often, physical periodic systems appear which contain only s and p atoms or which contain very limited numbers of molecules, such as homonuclear diatomic molecules and diatomic hydrides, oxides, and halides -- but in such cases one can judge that the investigator was being cautious due to lack of data or was presenting a simplified version for the sake of clarity, and that the ultimate goal was to include all of the \(N\)-atomic molecules.

By setting the value of one atom to null, the periodic systems for \(N\)-atomic molecules can be reduced to corresponding periodic systems for \((N-1)\)-atomic molecules, even though those molecules are not included in the original systems. In general, this process can be continued until an atomic periodic system is recovered. This atomic system (which may be quite different for different molecular periodic systems) will be called the originating periodic system.

As of this moment, only one book is known to have appeared which treats the subject of physical periodic systems.\(^{10}\)

3.2. Physical periodic systems of molecules

Periodic charts of the elements would be a physical system if atoms were considered to be molecules with \(N=1\). In this paper, however, \(N\) is defined to equal or exceed 2.

The first physical periodic systems of molecules were those of Clark, though he did not call them periodic systems. He classified diatomic molecules in two stages -- one in 1936 for hydrides\(^{11}\) and one, actually the year previous, for all other species\(^{12}\) — on the basis of the periodic behaviors of spectroscopic constants. Hydride molecules are arranged exactly as atoms in the atomic chart; other molecules \(AB\) are arranged in a series of two-dimensional tables, each of the series having atoms \(A\) from a different period of Clark's version of
the atomic table (Figs. 3,4). Clark also devoted a great deal of effort to showing that diatomic molecules with the same number of valence electrons (isoelectronic diatomic molecules) tend to have similar data.

That isoelectronic triatomic molecules tend not only to have similar properties, but also similar shapes, was already well known in 1953. In that year, Walsh explained why certain triatomic molecules are bent and others are linear, and why certain tetra-atomic molecules are planar and others are not, depending upon the total number of valence electrons. In order to do this, he extended Bohr's atombau prinzip to obtain an analogous principle for building up diatomic molecular-orbital configurations for triatomic molecules in such a way as to include their bond angles. This elegant theory coincides with observation in all but a few cases.\textsuperscript{13,14,15,16} In addition, it shows that triatomic molecules with a given frontier-electron structure occur periodically, with additional closed inner orbitals, as progressively heavier molecules are considered. Walsh could have suggested (but did not) that this periodic behavior could be the basis of a periodic system of triatomic molecules.

In 1971, at the 10\textsuperscript{th} Jubilee Mendeleev Congress in celebration of the 100\textsuperscript{th} year of Mendeleev's discovery, Syrkin\textsuperscript{17} presented portions of a periodic system for diatomic molecules. He had portions for homonuclear molecules and for hydride, oxide, sulfide, and fluoride molecules, each resembling the periodic chart of the elements (Fig. 5).

The Southern College (SC) entry into the field, in 1976, was remarkably similar to that of Syrkin.\textsuperscript{18} This was followed in 1979 by a complete periodic system for diatomic molecules.\textsuperscript{19} (The seeming rashness of including all possible diatomic molecules was defended by exhaustive graphical studies of all available orbital configurations and terms and of three spectroscopic properties of the molecules; since that time, something like 30 more properties have been investigated (unpublished).) The system consists of 15 three-dimensional blocks containing various combinations of atom series combined with themselves and with each other; the series of atoms correspond to those in rows of the chart of the elements. An algorithm for locating ionized molecules in the periodic system was also proposed. The work included many predictions of values for neutral main-group diatomic molecules.\textsuperscript{20,21}
Fig. 3. Clark's periodic chart of the elements. Used by permission from PERIODIC SYSTEMS AND THEIR RELATION TO THE SYSTEMATIC ANALYSIS OF MOLECULAR DATA, The Edwin Mellen Press, Lewiston, NY (Ref. 5).
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Fig. 4. One of the several similar tiles in Clark's periodic system of diatomic molecules, from Ref. 12.
Fig. 5. Two of Syrkin's tables, for oxides and for fluorides, from Ref. 17.
The procedure used resembled the cut-and-stack scenario of how Mendeleev constructed his periodic chart (Section 2). Diatomic-molecular data were plotted on two atomic number axes; consistent cyclic trends were observed in the graphs; the plane was cut into rectangles; similar rectangles were stacked (Figs. 6-8). The stacking of the rectangles is an important step, in that it made easily visualizable three-dimensional blocks out of a large array of rectangles. The best stacking order was later shown to be the product of the two period numbers of the atoms.

Monyakin's system consisted of three-dimensional blocks, as did the SC system of 1979. However, the placements of molecules with similar column indices and with similar row indices were exactly opposite (Fig. 9). This striking difference between seeming similar systems led directly to the idea of the matrix-product periodic systems in 1980 (Section 3.3).

Kong's (explicitly named) periodic systems with diatomic and main-group triatomic molecules are based on the concept that molecules are given group and period numbers which are sums of the group and period numbers of the constituent atoms. An article on the system with tetra-atomic molecular data is in progress. The systems necessarily resemble the periodic chart of the elements, since they are overlapped tilings of it. As an added elegant touch, the compartments of Kong's systems are enumerated, from upper left to lower right, by an (arbitrary) "molecular number" which serves the same useful role as does the atomic number in the chart of the elements. Kong presents many graphs and tables of various molecular data, showing a clear dependence on molecular group number and on molecular number.

The elegant simplicity of Kong's systems is somewhat deceptive in the sense that most of their compartments contain more than one molecule. For the diatomic case, Kong presents a table showing the contents of each compartment. The table uses the differences of the atomic group and period numbers, which shows that four independent variables are necessary to specify each individual diatomic molecule (Figs. 10, 11).

Kong's student, Huang, also began to construct a periodic table of triatomic molecules. He began the effort by writing the data for properties of molecules on cards and by arranging the cards such as to optimize the column and row behaviors, much as Mendeleev is said to have done. Kong participated
Fig. 6. The Cartesian lattice of diatomic molecules, with coordinates \( Z_1 \) and \( Z_2 \), speculatively extended to atomic number 118. The upper and right edges of the solid squares on the coordinate axes serve as decade makers. Vertical and horizontal lines are drawn just past the atomic magic numbers 2, 10, 18, 36, 54, and 86. Additional vertical and horizontal lines are drawn just before the beginnings of the transition-metal series (before atomic numbers 21, 39, 57, and 89), just past the ends of these series (after atomic numbers 30, 48, 80, and 112), just before the beginnings of the rare-earth series (before atomic numbers 58 and 90), and just past the ends of these series (after atomic numbers 71 and 103). If the lattice is cut along these lines, then various square and rectangular areas result. Similar areas are similarly hatched and labeled \( A \), through \( A_7 \), \( B_1 \) through \( B_7 \), and so on. Used by permission from PERIODIC SYSTEMS AND THEIR RELATION TO THE SYSTEMATIC ANALYSIS OF MOLECULAR DATA, The Edwin Mellen Press, Lewiston, NY (Ref. 5).
Fig. 7. The same as Fig. 6 except that similar areas have been stacked atop each other, that the areas with homonuclear molecules have been shorn of redundant heteronuclear molecules so that they are triangular instead of square, and that the interrupted pieces have been spliced together. Used by permission from PERIODIC SYSTEMS AND THEIR RELATION TO THE SYSTEMATIC ANALYSIS OF MOLECULAR DATA, The Edwin Mellen Press, Lewiston, NY (Ref. 5).
Fig. 8. Four blocks of the first SC complete cut-and-stack molecular periodic system. These four stacks are visible in Fig. 7. The names of the atoms from which molecules are formed are inscribed on the sides of the blocks; for instance, in layer 2 of block C, note the atoms K and Ca, and the atoms Ga to Kr. Ten transition-metal atoms have been removed from between them, as indicated by the short, heavy, vertical lines; molecules with such atoms are arranged in other blocks. The dashed and dotted outlines indicate how unipositive and doubly-positive ions should be translated so as to be in the same planes as neutral molecules with the same numbers of valence electrons. Used by permission from PERIODIC SYSTEMS AND THEIR RELATION TO THE SYSTEMATIC ANALYSIS OF MOLECULAR DATA, The Edwin Mellen Press, Lewiston, NY (Ref. 5).
Fig. 9. The $C_1+C_2=9$ block of Monyakin's periodic system. Used by permission from PERIODIC SYSTEMS AND THEIR RELATION TO THE SYSTEMATIC ANALYSIS OF MOLECULAR DATA, The Edwin Mellen Press, Lewiston, NY (Ref. 5).
Fig. 10. An illustration of how Kong's row-sum, column-sum periodic system is related to the atomic chart. The chart is shown as a heavy-line rectangle, with three of its atoms indicated as A, B, and C and with its center marked X. The center (X) of an identical copy is placed on A, traced (light lines), and the copy is filled with molecules AA, AB, AC, ... . The center (X) of another copy is placed on B (dashed lines), and the copy is filled with molecules BA, BB, BC, ... . The process continues until the center of the copies have been placed on every atom A, B, C, ... . Used by permission from PERIODIC SYSTEMS AND THEIR RELATION TO THE SYSTEMATIC ANALYSIS OF MOLECULAR DATA, The Edwin Mellen Press, Lewiston, NY (Ref. 5).
Fig. 11 (at right). Kong's periodic chart for diatomic molecules redrawn so as to create a three-dimensional periodic system. The system is symmetric front-to-back across a plane which has the shape of his periodic table (his Table 1). The structures in front and back are supplied with sufficient molecular symbols to allow easy comparison with Kong's Table 2. The top four layers of the three-dimensional system have \((R_1R_2) = (1,1), (1,1), (1,2), \text{ and } (2,2)\). The next three layers have \((R_1R_2) = (2,4) \text{ and } (3,3), (2,5) \text{ and } (3,4), \text{ and } (3,5) \text{ and } (4,4)\). The bottom two layers have \((R_1R_2) = (4,5) \text{ and } (5,5)\). Areas where \(R_1 \neq R_2\) contribute twice as many molecules to either side of the center (homonuclear) region as those where \(R_1 = R_2\). The drawing is shaded to the extent that all right-hand sides are blackened, but the shadows of those sides on front-facing or upward-facing sides are not shown. Vacant portions of Kong's Table 2 account for the alternate vacant volumes in the front and back structures of the system. These vacant volumes make the system approximately twice as thick from front to back as it would be otherwise. If it were not for this feature, and for the fact that the more ionically-bonded molecules were not included in Kong's table, the main portion of the system would closely resemble an octahedron with points at the corners of the central plane and at the front (dashed lines) and back.
heavily in completing the work, and in the end, the arrangement\textsuperscript{28} was very similar to Kong's but with the addition of transition-metal molecules.

Kaslin\textsuperscript{29} presented data on force constants for neutral diatomic molecules in a tiled series of tables, each of which has entries for diatomic molecules containing a given atom A. In each table, the entries for molecules AB arranged exactly as the atoms B are arranged in the chart of the elements.

### 3.3. Originating atomic charts and physical periodic systems

In 1970, Shchukarev suggested that the periodic chart of the atoms be a mathematical matrix and that molecules formed from these atoms would be arranged (in an incompletely defined way) in a supermatrix formed from this matrix.\textsuperscript{2} Other aspects of Shchukarev's work will be described in Section 4.2.

Independently of Shchukarev, the SC group considered the periodic chart of the atoms to be a matrix with rows $R$ and columns $C$. The outer product of this matrix with itself then produced a four-subscript $(R_1, C_1, R_2, C_2)$ matrix. This four-dimensional matrix formed a periodic system for diatomic molecules. Of course, it was immediately recognized that different originating atomic periodic tables would produce different four-dimensional diatomic systems.\textsuperscript{7} This process can be extended for larger numbers of atoms to create $2N$ dimensional systems for $iV$-atom molecules.

By taking two-dimensional slices ($R_1$ and $R_2$ constant) of this four-dimensional system and stacking them in order of increasing $R_1 R_2$ the three-dimensional cut-and-stack system of Hefferlin \textit{et al.} was reproduced. Similarly, Monyakin's three-dimensional system was reproduced by stacking slices with constant $C_1$ and $C_2$.

Kong's two-dimensional diatomic system can be reproduced by projecting the four-dimensional system into two dimensions ($R_1 + R_2$ and $C_1 + C_2$). Likewise, the projection of the six-dimensional system into the two dimensions $R_1 + R_2 + R_3$ and $C_1 + C_2 + C_3$ reproduces his triatomic system.

In Kaslin's work, given that atoms A and B are both associated with period and group numbers, it is clear that four dimensions are desirable to address diatomic molecules; each of his tables is a cut of the four-dimensional
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periodic system of diatomic molecules, and the cuts are arranged so as to be a two-dimensional tiled periodic system of diatomic molecules. Other interesting systems were formed through the use of different originating periodic tables. For instance, if the main-group elements are arranged in a series of concentric circles, the construction yields a series of tori with major radii equal to $R_1R_2$ (Fig. 12).

Thus, through appropriate manipulation of the originating periodic table and use of slice or projection techniques, the existent physical molecular periodic systems can be reproduced. Then it was natural to ask the question, "Can all possible physical periodic systems be generated by this methodology?" If the answer were yes, then we would have a good definition of physical periodic systems. That is, a physical periodic system for $N$-atom molecules is the outer $N$-product of an originating atomic periodic table, or can be generated from such a product system by use of cut-and-stack or projection techniques. The description to follow constitutes a test of the definition.

Several different pseudo-isoelectronic and isoelectronic diatomic and triatomic periodic systems have been created in an attempt to find an optimal system for isoelectronic molecules. For the pseudo-isoelectronic diatomic system, the three-dimensional projection system was defined by the axes $X=32(R_1-1)+32(R_2-1)+C_1+C_2$, $Y=R_1-R_2$, $Z=C_1-C_2$. The multiplier of 32 was used since the originating atomic periodic table was taken to be in long form. For medium form or short form originating periodic tables, the multiplier would be 18 or 8, respectively. This system has the advantage of putting all isoelectronic molecules into a small number of discrete slices of the $x$-axis. However, it does place molecules from several different isoelectronic series within the same slice (e.g. HCl and LiF), due to the existence of "gaps" within the originating periodic table. Thus the name "pseudo-isoelectronic."

The pseudo-isoelectronic $x$-axis was then replaced with a true isoelectronic axis defined by the total molecular electron number $n_e$. This system has the advantage of placing all molecules of a given electronic number on the same cross-section of the $x$-axis. However, the total electron number is not a simple function of row and column numbers. Thus, this system no longer can be generated by projection from a general four-dimensional system created from a simple originating periodic table. However, if the originating periodic table is taken to be three-dimensional, with the third dimension signifying
Fig. 12. Consider a periodic chart of the elements in which the eight-element series of s and p atoms lie on circles of radii $R_i$, and in which the elements from groups 1 through 8 lie at angles $\theta = 0, \pi/4, 2\pi/4, \ldots, 7\pi/4$. This periodic chart is squared into four dimensions. If $q_1$ and $q_2$ are held constant, the cuts are squares with coordinates $R_1$ and $R_2$, as in portions of the planes in Fig. 9. If $R_1$ and $R_2$ are held constant, the cuts are tori with coordinates $q_1$ and $q_2$, as shown in the figure [for $(R_1, R_2) = (2, 3)$]. The dashed line which spirals around the torus connects molecules with 20 electrons (and NeAr); the "circled" molecular symbols, which spiral around the torus in the opposite sense, contain atomic symbols which are isovalent.
atomic numbers, then this isoelectronic system can be reproduced by projection from the resulting six-dimensional product system. Thus, even esoteric isoelectronic systems obey the above definition for physical molecular periodic systems.

So far, geometrically-based physical molecular periodic systems have been examined, and a definition which includes all such systems has been achieved. However, alternative physical molecular periodic systems do exist; they are based on group dynamics.

3.4. Group-dynamical atomic and molecular physical periodic systems

Efforts to base the overall form of the periodic chart of the elements on group dynamical principles began in 1972, after it was found that the Fock group $SO(4)$ was able to reproduce the ordering of the energy levels of the hydrogen atom. The result was that the $SO(4)$ and a unitary group $SO(4,2)$ and a unitary group returns the periodic chart (including, for neutral atoms, the Madelung rules). Thus, atoms of all known elements were considered as state vectors of some abstract object.

The obvious next step was to extend the procedure to molecules. Zhuvikin (St. Petersburg University) and the Southern College group took up this challenge by considering the direct product of atomic $SO(3)XSU(2)$ multiplets as being a group multiplication. An effort to include the reality of atomic binding in molecules was made by the use of symmetrization and antisymmetrization operators.

This work has become much more rigorous. Atoms now are considered to be the results of creation operators acting on the vacuum state. The creation operators obey commutator relations appropriate to bosons, to conform to the fact any number of a given species of atom can exist in a molecule. Multiplets in the space $L(1)$ are described by the $SO(3)XSU(2)$ group [and others of the several groups or group combinations found in the chains related to $SO(4,2)XSU(2)$]. These multiplets are combined to obtain irreducible representations in spaces $L(2), L(3)$, etc. — i.e., diatomic, triatomic, etc., molecular state-vector multiplets - in the same symmetries. This is done by finding the seniority vector for a molecular multiplet and computing the other vectors symbolically by means of raising operators. This procedure identifies
the state vectors of the multiplet, many of them consisting of linear superpositions of individual molecular symbols.\textsuperscript{34,35} The symbolic computation of all multiplets of the periodic systems for diatomic molecules, and the enumeration of all the multiplets for triatomic molecules, based on the symmetries $SO(3) \times SU(2)$ and $SO(2,1)$, have now been completed.

Expressions for the expectation values of single-particle, two-particle, and higher-particle properties in the molecular state-vector basis can also be obtained symbolically. These expectation values can be evaluated numerically to the extent that the individual molecular data are available, and graphs of them can be plotted on the multiplet axes. The plots are very well-behaved and should allow surface-fitting and prediction of missing points. If there is only one missing molecular datum in the predicted expectation values, then their values can be obtained.

Group-theoretical periodic systems have the distinct advantage of having a firm dynamical basis; furthermore, the number of eigenvalue dimensions increases at most linearly as the numbers of atoms in the molecules increases. On the other hand, these systems have the disadvantages that a given state vector may include several molecules, and that any given molecule may appear dozens of times. The accuracy of predictions is a subject of current research at SC.

The work of Kamarov and Lyakhovskii on chemical periodic systems will be described in Section 4.2.

3.5 Work related to physical periodic systems

A great deal of research has gone into finding reduced (scaled to be similar) potential curves for diatomic molecules. Jenc is one of the leading figures in this research. His 1987 RPCs\textsuperscript{36} are not identical for all molecules, but show slight variations which are related to the groups and periods from which the atoms in the molecules come. For this reason, Jenc "loosely" calls these RPCs a periodic system of diatomic molecules.

In passing, it is interesting to mention the great deal of work which has gone into the study of hydrogenic energy levels, and of the periodic chart of the elements, in universes of other dimensions. The matrix-product method of
construction of molecular periodic systems can originate with such strange periodic charts.

4. Chemical periodic systems

4.1. Characteristics of chemical periodic systems

The distinguishing characteristic of chemical periodic systems is that they contain molecules with differing numbers of atoms. It is also a characteristic that they include only molecules stable under a well-known set of conditions (such as atmospheric-pressure wet chemistry) and which are therefore similar in the sense that common experimental techniques make possible the existence of data for large numbers of them (e.g., halogenated carbides and polycyclic aromatic hydro-carbons). It is a consequence of the second characteristic that rather accurate predictions can often be made for data of other molecules, within the particular class of molecules under consideration.

Quite commonly, these systems are supported with data which relate to chemical reactions; in some cases, the fundamental realities being classified are not molecules at all, but atom-atom bonds or functional groups. Molecular periodicity, as thus displayed, is closely related to the well-known "chemical similarity." The book of Johnson and Maggiora\textsuperscript{37} appears to dominate the field of chemical similarity, and it all but discusses chemical periodic systems. Such systems are discussed in Ref. 5, and in fact this paper is a revised version of Ref. 5, ch. 12.

4.2. Chemical periodic systems of molecules

Butlerov asserted\textsuperscript{38} that the French chemist A. Gerard created the first classification of compounds. Gerard played "patience" with bits of paper such as to place heterological and homological series of molecules in a natural arrangement. Newlands' contribution was dated 1862 (Fig. 1).

Morozov, in 1907,\textsuperscript{39} presented a table of hydrocarbon radicals, in a form almost in agreement with the table of the elements, and made a series of curious parallels between chemical elements and appropriate hydrocarbons (which he called "pseudo-elements"). These parallels resulted in the prediction
of the existence of a whole group of "non-valent" elements appearing as analogs of the paraffins; eventually these elements were found: the nobel gases!\textsuperscript{38}

Morozov's tables are beautifully done, many in elegant script and a few in tricolor. It is said that when Mendeleev read the book, he was so impressed with the contents that he immediately had Morozov appointed to a full professorship.\textsuperscript{38} Morozov did not always enjoy such "luck"; along with many other intellectuals in Czarist Russia, he suffered incarceration in the Schlisselburg Fortress.\textsuperscript{38}

In 1929, Grimm\textsuperscript{40} considered the set of hydrogen-displacement-law species (using for them Morozov's term, pseudo-elements) in a two-axis coordinate system: the valence, going from 1 through 4 for carbon through neon, and the number of hydrogen atoms (Fig. 2). Then he identified species which would result from combining these sets two at a time, placing them in a four-axis coordinate system which he called a "multidimensional table." The method is similar to that described in Section 4.3.

It is said that Shumyakin did similar work in Russia, and that there were hard feelings between them over the subject of credit for the discovery.\textsuperscript{38}

In 1967, Sanderson published a textbook\textsuperscript{41} with a unique chart of the elements, and similar charts for hydrogen, nitrogen, oxygen, sulfur, halide, methyl, ethyl, and phenyl compounds.

Shchukarev, in 1970\textsuperscript{2} and 1974,\textsuperscript{42} published scores of elaborate graphs showing how values of molecular properties (on the y axes) depend on the choice of molecule (on the x axes). Such graphs do not constitute a periodic system, nor did Shchukarev write of periodic systems of molecules, but the effort to demonstrate the periodicity is very evident. It is interesting that Mendeleev, Morozov, Shchukarev, and Sanderson all popularized the concept of molecular periodicity in textbooks.

Shchukarev seems to have come the closest to dealing with the different stoichiometries which are found in the liquid and solid phases. But even he did not show the way how to include such now-common compounds as FeO\textsubscript{1.1} or TiO\textsubscript{0.85}. 
In a series of five papers published from 1971 to 1973, Gorski developed a "morphological classification of simple species" which amounts to locating them in multi-dimensional spaces. Each coordination center and each ligand are described by five numbers (core charge, the number of core and valence electron shells, and tendency to participate in redox and acid-base reactions), though in certain cases some of these numbers may be omitted. Gorski does not claim that his classification is a periodic system.

In 1977, Martin drew some structures of hypervalent nonmetallic species, and called the figure a "partial periodic table."

In 1980, Hall proposed an "organic chemist's periodic table," with one axis for electron donors and another for electron acceptors. Examples of two kinds of compounds were placed in this coordinate system.

From 1982 and to the present time, Dias has worked out periodic tables, first for peri-condensed sextet benzenoids, then for a subset of these, i.e., total resonant sextet benzenoids, and then for indacenoid hydrocarbons. He also studied isomer enumeration, topological characteristics, an aufbau principle and excited internal structure concepts. Much of this work has been included in Dias' two "handbooks of polycyclic hydrocarbons."

Dias' constructions, of course, satisfy his elegant definition of a periodic system, as does Mendeleev's chart: a periodic table set is a partially-ordered set having as members some property X, (of objects 0 and of the operation <=, because these members are reflexive (X_i <=X_i), antisymmetric (if X_i <=X_j and X_j<=X_i, then X_i=X_j), and transitive (if X_i<=X_j and X_j<=X_k, then X_i<=X_k); it is a two-dimensional array; and it complies with the triad principle (any central element has properties which are the arithmetic means of properties of elements in either direction). A recent test of the triad principle on Mendeleev's chart is of interest. With a generalization to three dimensions, Dias' definition also applies to SC matrix-product periodic systems.

In 1982, 1983, and 1984, Haas published a brilliant new concept, the periodic system of functional groups. This classification can be considered as an imaginative extension of Grimm's hydrogen-displacement principle. First, he notes that fluorine can be substituted for the hydrogen in Grimm's
hydrogen displacement principle. And second, Haas points out that other halogens can play the same role as the fluorine, so that the hydrogen displacement principle becomes the element displacement principle. Third, he suggests that any radical with halogen-like properties (already known as pseudohalogens) can play the role as well - and then the resulting paraelements can again play the role (Fig. 13). And, fourth, he reminds us that the concept is not limited to the row-2 atoms but works with Si through Ar, Ge through Kr, Sn through Xe, and Pb through Rn. It can be seen that repeated pseudohalogen substitutions can make it possible to classify, and to make approximate predictions of the properties of, quite large and complicated molecules. That Haas is a world-renown expert on pseudohalogens put him in an excellent position to support the classification with numerical data.

It is possible to extend Haas' system to include all possible molecules. Fig. 14 shows how this extension would be done for row-2 diatomic molecules. The importance of such an extension to Haas' system is that it may be able to bridge the gap between chemical and physical periodic systems of molecules. It is clearly a chemical periodic system; at the same time, if the construction can be extended to include all TV-atom molecules, it would also become the totality of all physical periodic systems.

In 1986, Kamarov and Lyakhovskii presented their classification of halogenated carbides of the form $\text{CH}_j\text{F}_k\text{Cl}_l\text{Br}_m\text{I}_n$ where $j+k+l+p+q=4$. They plotted these species three dimensionally on the entropy, the total number of electrons, and $A$ (the sum of the differences between the electronegativities of the halogen atoms in the molecules and the electronegativity of hydrogen). This plot shows points arranged in (almost) straight lines corresponding to the repeated substitution of one halogen/hydrogen symbol for another. They also plotted some energies of the species against $A$. These plots show the same phenomena, and, when some predicted points are added, some of the same points are connected such as to suggest the tetrahedral form of multiplets in the symmetry $SU(5)$. The predicted points were apparently obtained with pseudo-additive formulae such as

$$E(\text{CH}_j\text{F}_k\text{Cl}\text{Br}_m\text{I}_n) = \left(1/4[jE(\text{CH}_4)+kE(\text{CF}_4)+lE(\text{CCl}_4)+mE(\text{CBr}_4)+nE(\text{Cl}_4)]\right),$$
Fig. 13. Haas' periodic system of functional groups. The first pair of diagrams shows how Haas generalized Grimm's hydrogen displacement principle by the substitution of fluorine for hydrogen; he names these species "paraelements." The second pair of diagrams shows how entries in the first pair of diagrams, in this case CF$_3$, can be substituted for the fluorine. Haas designates the resulting species "first-order derivative paraelements." The third pair of diagrams shows how entries in the second pair of diagrams, in this case CF$_3$S, can be substituted for the CF$_3$. Haas designates the resulting species "second-order derivative paraelements." The left-hand of the fourth pair of diagrams shows what happens if ligands like oxygen, sulfur, or nitrogen are used; displacements of two or three groups must take place. The right-hand of the fourth pair of diagrams shows what happens if various of the paraelements of the left-hand diagram are substituted with the appropriate displacements. The diagrams are from Ref. 64; used with permission.
where $E$ refers to the heat capacity or to other properties. Kamarov and Lyakhovskii took the dramatic step of applying the theory of $SU(5)$ groups to these molecules. They considered the vectors H, F, Cl, Br, I to be the irreducible representation in the space $L(1)$ of atoms, and then constructed irreducible representations in $L(4)$, the space of the five-atom species being studied (the carbon atom being understood).

The classification of molecules has fascinated Russian chemists ever since the time of Mendeleev. "A Systematic Approach to Researching Properties of Solutions"\textsuperscript{66} and "The Kinetic and Thermodynamic Law-abiding Behavior of Interactions of Atomic and Molecular Halogens with Fluorinated Radicals in the Gas Phase"\textsuperscript{67} are typical recent thesis topics in the Chemistry Department at St. Petersburg University, and Voskresensky presented "The Natural Quantum Chemical System of Organic Compounds," clearly a periodic system, at WATOC World Congress in Toronto\textsuperscript{68} -- all of this in 1990!

4.3. Work related to chemical periodic systems

Shigorin\textsuperscript{69,70,71} developed an elaborate molecular classification scheme based on their luminescence spectra.

Schulz\textsuperscript{72} has used category theory to describe reactions involving stoichiometric entities. Many brilliant advances in analyzing molecular structures have been made by other investigators, using combinatorics, topology, and graph theory. When carried to maturity, these methods may well allow for extending or complementing chemical periodic systems (e.g., King's\textsuperscript{73} "Eplacarnet Tree," where eplacarnet is short for elemental planar carbon networks).

Many other works, such as Sato's elaborate classification of tecto-silicates,\textsuperscript{74} look very much like chemical periodic systems.

5. Discussion

Characteristics of physical and chemical molecular periodic systems have been presented in Sections 3.1 and 4.1. A rigorous definition of physical periodic systems has been provided in Section 3.3.
A variety of *ad-hoc* ideas have been mentioned during the course of this review: writing data for molecules on cards and moving the cards into optimal positions [Gerard, Mendeleev(?), Huang]; tiling arrangements of oxides, fluorides, and the like [Clark, Kaslin]; and cutting and stacking portions of a plane [Southern College group]. Two methods with sound theoretical bases have also been described: the matrix-multiplication of an originating periodic chart of the elements, followed by slicing or projection; and the use of group dynamics.

6. **Recommendation**

In light of the rapidity with which interest in classifications of molecules is growing, including the construction of various kinds of periodic systems, we recommend the use of the characteristics of the two kinds of systems as a test of which appellation to use.

Specifically, we recommend the term *Physical Periodic System of Molecules* if the construction has only molecules with the same number of atoms (and which include, or can easily be extended to include, all possible molecules with that number of atoms). The term *Chemical Periodic System*, by contrast, should be used for all systems including various numbers of atoms or which are confined in scope to include only a limited class of atoms (e.g., those obeying the octet rule). Randic is to be commended for the choice of name for his recent "Periodic Table of Octane Isomers"; the name is sufficiently self-explanatory that the adjective "Chemical" is not needed.

It is possible to arrange molecules in coordinate systems which are irrelevant to periodicity, e.g., a Schweinler lattice. We would not recommend that the term Periodic System be ascribed to such arrangements, no matter how elegant they might be.
References


10. Ref. 5.


21. Ref. 5, pp. 4, 226, and ch. 7.


23. Ref. 5, pp. xxiii-xxxiv and ch. 12, set. 2.

24. Ref. 5, ch. 6, set. 7.
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27. Ref. 5, ch. 11.


76. Ref. 5, pp. 124-126, 128.