

The Dual Sense of the Term “Element,” Attempts to Derive the Madelung Rule, and the Optimal Form of the Periodic Table, If Any

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ABSTRACT: This article concerns various foundational aspects of the periodic system of the elements. These issues include the dual nature of the concept of an “element” to include element as a “basic substance” and as a “simple substance.” We will discuss the question of whether there is an optimal form of the periodic table, including whether the left-step table fulfills this role. We will also discuss the derivation or explanation of the $[n + \ell, n]$ or Madelung rule for electron-shell filling and whether indeed it is important to attempt to derive this rule from first principles. In particular, we examine the views of two chemists, Henry Bent and Eugen Schwarz, who have independently addressed many of these issues. © 2008 Wiley Periodicals, Inc. *Int J Quantum Chem* 109: 959–971, 2009

Key words: elements; periodic table; Madelung rule; left-step table

The Nature of the Concept of an “Element”

Discussions concerning the fundamental importance of the concept of “element” have been published by a number of historians and philosophers of chemistry in recent years [1–5]. In addition, some chemists have begun to elaborate their

views on the subject [6, 7]. Much of this work appeals to the published views of Mendeleev in the late 19th century and also to the work of Paneth in the 1920s and 30s [8]. Some authors began at the dawn of ancient Greek philosophy, in which there was considerable discussion upon the most fundamental components of the nature [9].

However, this article will take as its starting point the seminal work of Lavoisier [10]. It is generally agreed that Lavoisier was among the first chemists to turn their backs on regarding the elements as unobservable principles or as literally substances which

stand underneath all matter.¹ In common with the growing positivism that characterized the scientific revolution in general, Lavoisier's approach was to eschew any notions of elements as principles in favor of regarding the elements as "simple bodies" to use an English translation of his own term *corps simples*.² These "elements" were regarded as substances which could actually be isolated and which were the final stage of any attempts to break them down into further components.

In 1789, Lavoisier and his collaborators famously published their list of elements as simple bodies. In doing so they continued to include a number of "principles" such as *chaleur* and *lumière*, but it seems to be widely held that their intention was to concentrate on the truly simple bodies. As is the case in many revolutionary changes, including coincidentally the French revolution that took the life of Lavoisier, such tumultuous changes have a tendency to be excessive in their early stages. It was not until the writings of Mendeleev, a good 80 years later, that the more abstract sense of the term "element" was to return and to receive a clear elaboration, although it became rather different from the "principles" of the ancient Greek philosophers and the alchemists. For example, Mendeleev wrote

It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogeneous substance, and as a *material* but invisible *part* of a compound. Mercury oxide does not contain two simple bodies, a gas and a metal, but two elements, mercury and oxygen, which, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is contained in mercury oxide; it only contains the substance of the elements, just as steam only contains the substance of ice, but not ice itself, or as corn contains the substance of the seed but not the seed itself [12, 13].

The subsequent development of atomic theory and quantum mechanics has provided an explana-

¹There has been some discussion as to whether the word "substance" is appropriate in this context. For example, Earley believes it is not because it implies a form of materiality which is not intended [2]. In this article, the word "substance" will be used, however, because of the terminology coined by Paneth when he drew his distinction between the two senses of the term "element." However, Paneth actually uses the German words "grundstoff" and "einfacherstoff" which were translated as basic substance and simple substance, respectively, in the article that appeared in the *British Journal for the Philosophy of Science* and which has been most widely read.

²This view is opposed by [11].

tion for the periodic table and a shift of attention away from macroscopic chemical properties to the properties of the neutral atoms of the elements. One result of this shift in attention has been that Mendeleev's distinction, having to do with macroscopic chemical elements, has been all but completely forgotten.

However, an important development within atomic physics, namely the discovery of isotopy in the 1910s, led some philosophically minded chemists to reexamine Mendeleev's distinction and to rehabilitate it in a modified form. With the rapid discovery of isotopes it began to seem as though there were far more "elements" than the ~90 or so which were displayed on periodic tables at the time. The work of Soddy [14], in particular, served to clarify the situation, and one that had been anticipated by Crookes,

I conceive that when we say the atomic weight of calcium is 40, we really explain the fact, while the *majority* of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on [15].

But what would become of Mendeleev's periodic system which now seemed to consist of 300 or so "elements"? To some chemists, the discovery of isotopes implied the end of the periodic system as it was known.³ These chemists suggested that it would be necessary to consider the individual new isotopes as the new "elements." But the chemist Paneth adopted a less reductionist approach, arguing that the periodic table of the familiar chemical elements should be retained because it dealt with the "elements" that were of interest to chemists. A justification for this view was provided by the fact that, with a few exceptions, the chemical properties of isotopes of the same element are indistinguishable.⁴ Moreover, Paneth appealed to Mendeleev's distinction between the two senses of the concept of an "element" in order to provide a philosophical rationale for the retention of the chemist's periodic table. Paneth argued that the discovery of isotopes of the elements represents the discovery of new elements as simple substances, whereas periodic

³This kind of argument was given by Ida Noddack, for example, as described by Van Tiggelen [16].

⁴This fact was verified experimentally by Paneth and Hevesy, who found that the redox potentials of bismuth cells containing different isotopes of the metal produced indistinguishable values.

classification à la Mendeleev should be concerned with elements as basic substances.⁵

Much more recently it has been suggested that the key to Mendeleev's success, when compared with his competitors like Lothar Meyer, lay precisely in the former's adherence to this philosophical distinction [17]. Even more recently some authors have suggested that the distinction might play a role in the question of the placement of the elements hydrogen and helium in the periodic system [6, 18].⁶

Optimal Form, If Any, of the Periodic Table

There have been, quite literally, over 1,000 different periodic tables published since the early forms by Lothar Meyer, Mendeleev, and other early pioneers [18]. Amateur and professional scientists alike, frequently debate the "best form" of the periodic table. On the other hand, many chemists adopt a somewhat condescending attitude to such activities while maintaining that there is no such thing as an optimal periodic table, adding that different forms only serve to highlight different aspects of the properties of the elements. These chemists thus seem to be placing a greater premium on utility than on "truth" for want of a better word. Such apparent conventionalism, among many chemists, not to say relativism, is surprising at least to the present author. This is especially so because these same chemists are quick to pour scorn on any suggestion of relativism in science in general, of the type that was so well criticized by Gross and Levitt and more recently by Sokal [19, 20]. While the relativists are frequently perceived as being on the losing side of the Science Wars and are ridiculed by the majority of the scientific community, the notion that periodic classification is a matter of subjectivity does not generally meet with any criticism. This ambivalent tendency is even true among authors who argue strenuously for one particular form of the periodic table such as that of Bent, of whom more will be said presently [21].⁷

⁵Indeed, the terminology of element as basic substance as opposed to as simple substance, which has been used throughout this article, originates with this work of Paneth.

⁶However, I believe that Bent's understanding of elements as basic substances is incorrect because he insists on identifying them with neutral atoms of the elements.

⁷See review of Bent's book by Schwartz [22].

Of course it is important to distinguish between the shape of the periodic table, which is admittedly a matter of choice or convention, from tables that actually place certain elements in different groups. The point is not whether one should favor a tabular form, in which periods end abruptly, over circular displays which emphasize the continuity of the sequence of the elements for example. The question is rather whether to favor a table that places the element helium among the noble gases, when compared with tables that place this element among the alkaline earths. The wider question is whether elemental classification is an objective matter of fact or whether it is a matter of convention. It is the question of whether helium, for example, has a natural kinship with the noble gases or with the alkaline earths. Or as philosophers of science are apt to say, it is the question of whether or not groups, or families of elements, represent *natural kinds*.

In this article it will be argued that the classification of the elements is an objective feature of the world and not open to conventional choice and relativism. It will also be argued that the element helium belongs objectively and most naturally either to the alkaline earths or the noble gases regardless of whether such a question may be settled at present.⁸

The Left-Step Table

This form of the periodic table is shown in Figure 1. Although it is often assumed to have a quantum mechanical origin it was first proposed on purely esthetic grounds by the Frenchman, Charles Janet [23]. But in a quantum mechanical guise it takes on a new lease of life, as will be explained shortly.

If one accepts the modern reductionist tendency that explanations of chemical facts are to be found at the level of electronic configurations, it is tempting to regard the element helium as an s-block element and perhaps to move it into the s-block of the periodic table. This change in the position of helium represents one important feature of the left-step table. A second feature is a movement of the entire s-block, complete with relocated helium, to the right edge of the conventional periodic table. In this way one achieves a pleasingly regular shape with no apparent gaps between sets of elements such as beryllium and boron, or magnesium and

⁸The answer to this question favored by the present author is postponed for the time being.

															H	He	
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

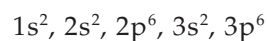
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

FIGURE 2. Medium-long form periodic table.

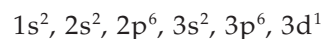
of m are $-2, -1, 0, +1, +2$. Finally, the fourth quantum number labeled m_s can only take two possible values, either $+1/2$ or $-1/2$ units of spin angular momentum. We thus have a hierarchy of related values for the four quantum numbers, which are used to describe any particular electron in an atom. These relationships are derived theoretically and do not involve the use of any experimental data.

For example, if the first quantum number is 3 the second quantum number ℓ can take values of 2, 1, or 0. Each of these values of ℓ will generate a number of possible values of m_ℓ and each of these values will be multiplied by a factor of two since the fourth quantum number can adopt values of $1/2$ or $-1/2$. As a result there will be a total of $2n^2$ or 18 electrons in the third shell. This scheme thus explains why there will be a maximum total of 2, 8, 18, 32, etc., electrons in successive shells as one moves further away from the nucleus.

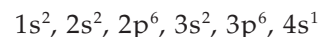
But does the fact that the third shell can contain 18 electrons also explain why some of the periods in the periodic system contain eighteen places? Actually not exactly. If electron shells were filled in a strictly sequential manner the explanation would be complete. But as anyone who has studied even just high school chemistry is aware, the electron shells do not fill in the expected sequential manner. The configuration of element number 18, or argon is



This might lead one to think that the configuration for the subsequent element, number 19, or potassium, would be



because up to this point the pattern has been to add the new electron to the next available orbital in the sequence of orbitals at increasing distances from the nucleus. However, experimental evidence shows that the configuration of potassium should be denoted as



One of the authors to ask whether a theoretical derivation of the $n + \ell$ rule might be found was the late Per Olov Löwdin, who wrote

The energy rule for the neutral atoms was obviously in contradiction to Bohr's calculation on the hydrogen atom, which indicated that the energies should be increasing with increasing n . It is typical of the nature of "frontier-research" that Bohr abandoned this rule for the higher atoms, since it led to the wrong structure of the periodic system, and the modified rule $[(n + \ell, n)]$ seems to have

been obtained in a more intuitive way. Bohr himself was never too explicit about his “Aufbau”-principle, and [the rule] is sometimes referred to as the Goudsmit-rule or the Bose-rule. It is perhaps remarkable that, in axiomatic quantum theory, the simple energy rule has not yet been derived from first principles ([24], p 332).

There have been a number of attempts to meet the “Löwdin challenge,” as it has been called. Allen and Knight published an explanation in the *International Journal of Quantum Chemistry*, which has turned out to be rather problematic as I have recently argued [25–27]. In addition, Ostrovsky has published an account in which he claims to explain the $n + \ell$ rule, but this account is far from transparent, or convincing, at least to this author [28].

Recent Developments

The preceding survey will serve as background for two recently published accounts which touch on all four of the various aspects of the periodic system that have been reviewed above.

In the July 2007 issue of the *Journal of Chemical Education* Bent and Weinhold, an inorganic and a theoretical chemist, respectively, published an extensive paper on the left-step periodic table. One rather noticeable feature of their article is the overtly reductionist stance that the authors adopt. They wrote

Only with Bohr’s 1913–1923 introduction of the “old quantum theory” (itself strongly inspired by chemical periodicity patterns; vide infra) and the final discovery of Schrödinger’s wave mechanics in 1925 would the periodic table be supplanted as the deepest expression of current chemical understanding ([21], p 2).

It seems a little excessive, at least to this author, that the periodic table is being regarded as somehow supplanted by quantum mechanics. This is something that is simply not the case on closer examination, as I have argued in some previous articles [29, 30].

Or to cite another passage, Bent and Weinhold wrote

Modern *ab initio* calculations daily confirm the usefulness of the orbital-based quantal perspective as a basis for predicting complex chemical phenomena. In this framework the fundamental descriptors of the orbital filling sequence are the

radial (n) and angular (l) quantum numbers. Thus, one may conclude that the most profound characterization of the chemical properties of a given atom is in terms of quantum numbers or equivalent descriptors that allow the relative energy, angular shape, radial diffuseness, or other properties of its occupied and unoccupied valence orbitals to be inferred ([21], p 3).

It is not easy to see why the authors believe that the success of orbital calculations should lead one to think that the most profound characterization of the properties of atoms implies such an importance to quantum numbers as they are claiming. As is well known in quantum chemistry, successful mathematical modeling may be achieved via any number of types of basis functions such as plane waves. Similarly, it would be a mistake to infer that the terms characterizing such plane wave expansions are of crucial importance in characterizing the behavior of atoms.

A third quotation to illustrate the naively reductionist approach of Bent and Weinhold is as follows:

A primary goal of the periodic table is to assist recognition of the ground-state valence electron configuration of each atom, the chief determinant of its chemical properties” ([21], p 5).

While it may be true that the periodic table is used in chemical education in order to arrive at the electronic configuration of any particular atom, this is surely not a primary goal of the periodic table for chemists in general. The main goal of the periodic table remains as the classification scheme for the properties of the elements, especially as they occur in chemical compounds.⁹

Of course, a more charitable interpretation of Bent and Weinhold’s statement might be to emphasize that quantum mechanics provides an approximate explanation for the periodic table, whereas the periodic table itself was merely a successful classification awaiting a theoretical explanation. But one cannot help thinking that this interpretation is not what the authors had in mind. What they intended

⁹In other words, the element as a basic substance. The similarity between the elements occurring in the same group of the periodic table is not always obvious if one focuses on the elements as simple substances. For example, consider the halogens. Who would think of grouping together such a diverse set of simple substances as two green-yellow gases, a brown liquid, and a violet-black solid? And yet the compounds of these four halogens with sodium, for example, are all very similar white crystalline solids.

was apparently the notion that all that really matters are the microscopic “goings on.”

But the reductionist approach adopted by Bent and Weinhold is nevertheless consistent with their wanting to explain the periodic table through the properties of the neutral atoms of the elements rather than their macroscopic properties.

Bent and Weinhold on the $n + \ell$ rule

One of the main benefits of the paper by Bent and Weinhold is a plausible explanation for the $n + \ell$ rule which does not, at first sight, seem to suffer from the drawbacks of the explanations of Allen and Knight as well as Ostrovsky. However, the recent explanation by Bent and Weinhold comes at a certain cost as will be explained.

The authors begin by appealing to the Sturm-Liouville theory which applies to a wide class of differential equations. This theory essentially holds that the solutions to this class of differential equations can be placed in order of increasing energy according to the number of nodes that they possess. This notion appears to be rather promising given that orbitals with increasing values of n and ℓ are indeed known to have an increasing number of radial as well as angular nodes with a corresponding increase in orbital energy.

But the promise of simplicity is somewhat short-lived once one realizes that the total number of nodes in atomic orbitals, as normally defined, fail to predict the correct order of increasing energy. The 4s orbital has 3 radial nodes plus 0 angular nodes, making a total of 3 nodes altogether. Meanwhile, the 3d orbital has 0 radial nodes and 2 angular nodes and thus a total of only 2 nodes. And yet the 4s orbital with the higher total number of nodes is preferentially occupied or has a lower energy than the 3d orbital.

However, the authors soon inform the reader that they are adopting a rather exotic sense of the term radial node, as well as treating the angular nodes in an unconventional manner. In addition to the radial nodes, given by the well-known equation of $n - \ell - 1$, the authors include an additional radial node because of the existence of a node at infinity. The result of this change is to produce a total of $n - \ell$ radial nodes.

Next, instead of counting the normal number of angular nodes, or ℓ , the authors consider twice the value of ℓ . The net result of both of these changes is to give $n - \ell + 2\ell$ or a total of $n + \ell$. Not

surprisingly they thereby obtain some consistency with the $n + \ell$ rule, and the number of nodes with increasing energy, by using this very specific way of counting the nodes in any particular atomic orbital. For example, the 4s orbital has 3 radial nodes plus 1, plus 0 angular nodes, making a total of 4 nodes if counted in this particular manner. Meanwhile, the 3d orbital has 0 radial nodes plus 1, plus 2 times 2, giving a total of 5 nodes when counted in the same manner.

As a result of this way of counting nodes the 4s orbital has a lower total number of nodes, that is, 4 when compared with 5 in the case of the 3d orbital. Moreover, this order agrees with the experimentally observed order whereby 4s has lower energy than 3d.¹⁰ However, whether this is a satisfactory first principles explanation of the $n + \ell$ rule, which meets the Löwdin challenge, is something that seems rather unlikely given the ad hoc nature of the manner in which nodes have been counted.

It should also be said that the reason why Bent and Weinhold devote such attention to the $n + \ell$ rule is that, as mentioned earlier, the rule is clearly represented on the left-step table, the form of the periodic table that they favor. In addition, as was mentioned, the authors believe that the best representation of the periodic system should be based on the electronic structure of the neutral atoms of all the elements and not on their macroscopic properties.

The Concept of “Element” Revisited

But what does all this work have to do with the question of the interpretation of the concept of an “element”? This issue is not explicitly addressed in the paper by Bent and Weinhold but has been addressed by Bent in his recent book, which is entirely devoted to the left-step table [6].

Bent claims that the periodic system should be primarily based on the structure of neutral atoms rather than on macroscopic properties of the elements. In doing so he claims support from none other than Mendeleev. Bent also claims to garner support from the writings of Mendeleev in steering clear of the properties of the elements as simple substances in crucial matters of classification of the elements. In fact, the identification of elements as basic substances with the atoms of the elements is

¹⁰This is the case for K and Ca but not for subsequent transition metal atoms [31].

indeed suggested by a number of passages in the writings of Mendeleev, which are duly cited by Bent.

For example, Bent cites what he calls Mendeleev's absolute distinction:

The central idea that aided me in undertaking the study of the periodic law of the elements, consists primarily in the absolute distinction between an atom [of e.g. the element carbon] and a simple body [such as diamond or graphite] ([32, p 193]).

All that I am going to say [about the Periodic Law] must be understood as relating to atoms... and not simple bodies ([32, p 193]).

But I would like to suggest that Mendeleev, and now Bent, are incorrect in drawing this identification. Nor do I claim any originality in pointing out Mendeleev's error because this was already clearly stated by Paneth in a couple of articles written in the 1930s.

The reason why this distinction [two senses of "element"] has been so little noticed seems to be, on one hand, that the terms used by Mendeleeff are not very appropriate, and that, on the other hand, by coupling them to the pair of concepts, molecule and atom, he seems to have missed the essential point ([33], p 57).

It is hardly possible in chemistry to introduce a contrast between elements and simple bodies, as the definition of element since Lavoisier is based on the simple body. It seems to me to be even less apt simply to equate the terms element/atom and simple body/molecule, respectively for apart from the fact that there are simple bodies whose molecules are single atoms, molecules and atoms belong indubitably to one and the same group of scientific concepts, while the essential difference between element and simple body in the Mendeleeffian sense of the words, lies in their belonging to quite different spheres in epistemology ([33], p 57).

To remedy this mistaken identification I propose a return to discussing elements as basic substances, without recourse to any microscopic account.

A Paper by Schwarz

I now proceed to an examination of a second recent paper by the German theoretical chemist Schwarz which was published in Foundations of

Chemistry [7]. This paper I believe is more philosophically astute than the work of Bent and Weinhold or the book by Bent.

Schwarz addresses the question of the concept of an "element" directly and concludes that an element may be regarded not in just two, but three ways.

1. Basic chemical element: The original and still present meaning of element or principle in chemistry is the basic sub-stance behind chemical stuffs, only implicitly defined through a conservation law in chemical reactions.
2. Metallurgical element or simple material: The chemical stuff that contains only one CE. It is specified through the stationary physical properties of its different phases and modifications.
3. Astrophysical spectroscopic element or elemental atom: Physical atoms in vacuum specified by the nuclear charge.

The CEs, however, refer to the properties and reactions of macroscopic materials, made up of chemically *deformed* atoms ([7], p 142).

It immediately becomes clear from this list that Schwarz is not falling into the error of identifying elements as basic substances with the neutral atoms of the elements, given that he includes the neutral atoms as a third sense of element in addition to basic substances and simple substances.

Indeed the article by Schwarz is even more radical, in that he considers the attention that has been devoted to trying to derive the $n + \ell$ rule to be entirely misplaced.

There are two basic differences of (sic) free atoms and chemically bound atoms. First, the more diffuse an AO, the stronger it is perturbed in molecular and condensed matter. The $(n + \ell)$ s AOs of the transition metal atoms, especially of the earlier ones, are not of primary importance for chemical bonding. Their relevance is comparable to that of the diffuse orbitals of main group elements ([34], p 653).

Second, metal atoms carry some positive charge in the majority of their compounds. Transition metal cations have pure d configurations, in contrast to the mixed d-s configurations of free neutral transition metal atoms. There is the chemical rule that "s electrons fall down into the d level

when chemical bonding occurs.” The wide field of organic, inorganic and biochemical transition metal complexes is semi-quantitatively explained by pure d-bonding. This holds even for nonpolar complexes. For instance, while the ground configuration of the Ni atom in its neutral free state is d^9s^1 , the valence configuration of Ni in the famous homopolar $Ni(CO)_4$ complex is d^{10} ([34], p 653).

There is no obvious logical or physical relation between the configurations of the neutral atomic ground states and the main chemical characteristics of the elements ([34], p 653).

During the endeavor to understand and explain the PT physically, a lot of effort has been spent on secondary problems. Even worse, an orbital ordering rule that has no general validity, has been assumed to be of central relevance. It has often been said that the structure of the neutral atoms is of primary importance for the periodic system. This is true, though in a modified sense ([34], p 653).

What is of primary importance chemically is not the ground state, nor the ground configuration, which is some average of valence states, of the free atom; but it is the atomic response properties to perturbations by other atoms. That is governed by the energies and spatial extensions and polarizabilities of the upper core and of the compact valence orbitals ([34], p 653).

What Schwarz appears to be implying, although this is nowhere stated explicitly, is the following parallel between the elements as basic and simple substances at both the macroscopic and microscopic levels.

Macroscopic	Microscopic
Elements as basic substances	Bonded atoms
Elements as simple substances	Neutral atoms

I believe this to be a step in the right direction, in that it avoids the identification of basic substances and neutral atoms, but still not a completely consistent picture. It is a step in the right direction since it focuses attention on bonded atoms rather than isolated neutral atoms and thus in keeping with the notion that the periodic system classifies the elements as they occur in compounds rather than in isolation.

Because Schwarz avoids the identification between elements as basic substances and neutral at-

oms, he is less willing to regard the derivation or otherwise of the $n + \ell$ rule as an important feature of the microscopic understanding of the periodic system. As Schwarz repeatedly stresses, the order of electron-shell filling in ions does not follow an $n + \ell$ rule but the simpler n rule.

Exceptions to the $n + \ell$ rule

In any case, as many authors have previously pointed out the $n + \ell$ rule is strictly speaking subject to about 20 exceptions, thus further hinting that it has no fundamental value.¹¹ The best known of these anomalies occur in the neutral atoms of chromium and copper which have the following expected and observed electronic configurations, which generations of general chemistry student have been obliged to learn:

	Expected configuration	Observed configuration
Chromium	$[Ar] 4s^2 3d^4$	$[Ar] 4s^1 3d^5$
Copper	$[Ar] 4s^2 3d^9$	$[Ar] 4s^1 3d^{10}$

The second transition series shows a total of six anomalous configurations:

	Expected configuration	Observed configuration
Niobium	$[Kr] 5s^2 4d^3$	$[Kr] 5s^1 4d^4$
Molybdenum	$[Kr] 5s^2 4d^4$	$[Kr] 5s^1 4d^5$
Ruthenium	$[Kr] 5s^2 4d^6$	$[Kr] 5s^1 4d^7$
Rhodium	$[Kr] 5s^2 4d^7$	$[Kr] 5s^1 4d^8$
Palladium	$[Kr] 5s^2 4d^8$	$[Kr] 5s^0 4d^{10}$
Silver	$[Kr] 5s^2 4d^9$	$[Kr] 5s^1 4d^{10}$

while there are two such anomalies in the third transition metal series:

	Expected configuration	Observed configuration
Platinum	$[Xe] 6s^2 5d^8$	$[Xe] 6s^1 5d^9$
Gold	$[Xe] 6s^2 5d^9$	$[Xe] 6s^1 5d^{10}$

The symbols for all these elements showing anomalous configurations are shown in boldface in Figure 3.

¹¹These 20 cases do not represent anomalies to the order of orbital filling which is invariably governed by the $n + \ell$ rule but are anomalous in the sense that the s orbital is not completely filled before the corresponding d orbital begins to fill.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	T	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

FIGURE 3. Medium-long form table highlighting elements with 10 anomalous configurations (in bold face) among 30 the d-block elements.

What would happen if we were to take up Schwarz's suggestion on concentrating on bonded atoms rather than neutral atoms, which do not occur in bonded transition metal atoms? What kind of periodic table would one be led to?¹² For example, one might examine the electronic configurations of the highest and most common oxidation states for each of these metals. This is carried out in Figure 4, below, in which we find that of the 10 anomalous neutral atom configurations, only two remain anomalous in the sense of differing from the configurations of other metal ions in their respective groups. Whereas the Cu^{+2} ion has configuration $[\text{Ar}] 3d^9$, those of the Ag^+ and Au^{3+} ions are $[\text{Kr}] 4d^{10}$ and $[\text{Xe}] 5d^8$.

However, Schwarz's suggestion to focus on bonded atoms rather than neutral atoms also runs into a major problem because the atoms of any element typically show a large variety of oxidation states. For example, atoms of chlorine occur in the zero oxidation state in the chlorine molecule, the -1 state in NaCl , $+1$ in HOCl , $+3$ in HClO_2 , $+5$ in HClO_3 , and $+7$ in HClO_4 .

To devise a periodic table of configurations of bonded atoms we would be obliged to focus on perhaps the highest oxidation state or the lowest oxidation state. Such decisions would not appear to

be sufficiently categorical. Unfortunately one must abandon the notion that the problem may be solved by merely switching attention from neutral atoms to bonded atoms of the elements, as Schwarz seems to be recommending. A more satisfactory solution to such questions must surely be sought elsewhere.

A Possible Solution

It was suggested earlier that Schwarz's identification of bonded atoms with elements as basic substances represents a step in the right direction. This notion will now be examined more carefully, since it too will be found lacking in a rather fundamental way, which was hinted at in some earlier quotations from Paneth. The concern voiced by Paneth regarding associating elements as basic substances with neutral atoms was due to the fact that these concepts inhabit different epistemological levels. This is equally true of the identification of elements as basic substances with bonded atoms, which is the identification that Schwarz supports.

Instead of identifying elements as basic substances with neutral atoms (Bent and Weinhold and almost everybody else) or elements as basic substances with bonded atoms (Schwarz), I would like to propose just focusing on elements as basic substances in Paneth's macroscopic sense. The one ma-

¹²This question has not been pursued by Schwarz.

H																		He
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc +3	Ti +4	V +5	Cr +6	Mn +7	Fe +3	Co +3	Ni +3	Cu +2	Zn +2	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y +3	Zr +4	Nb +5	Mo +6	Tc +7	Ru +3	Rh +3	Pd +3	Ag +1	Cd +2	In	Sn	Sb	Te	I	Xe	
Cs	Ba	Lu +3	Hf +4	Ta +5	W +6	Re +7	Os +3	Ir +3	Pt +3	Au +3	Hg +2	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	112							

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

FIGURE 4. Medium-long form table showing highest and most common oxidation states of the d-block elements. Only two of these 30 ions, Ag^{+1} and Au^{+3} , (shown in bold-face) show anomalous electronic configurations with respect to other ions in the same groups.

major characteristic of such a sense of the term “element,” as we have discussed earlier, is simply its atomic number. It is something of a paradox that even in modern chemistry where we have learned that electrons are responsible for all manner of reactivity, be it electron transfer, sharing, or exchange of various kinds, one is nevertheless forced into conceding that the identity of any element resides in the unchanging nuclear charge and not in the electrons.

Seen from a somewhat different perspective this fact should not seem at all paradoxical, because in seeking identity one needs to focus precisely on what does not change. But how can the mere value

of Z , or some function of it, be used in the classification of the elements into groups? Of course, the use of atomic number in arranging the elements into a sequence (primary classification) has been appreciated in the pioneering work of van der Broek and Moseley (see Chapter 6 in [18]).

What will now be proposed is that in addition to its role in ordering the elements, the quantity Z may be used to also affect a secondary classification of the elements, that is, their placement into vertical groups in the sense of the conventional periodic table. In proposing this idea, I make use of what was historically the earliest hint of chemical periodicity, namely, the existence of triads of elements [35].

The realization that the better ordering criterion is atomic number rather than atomic weight invites us to consider triads of atomic numbers. This reveals a most remarkable fact, namely that ~50% of all conceivable triads on a conventional periodic table are in fact exact. For example, the elements sulfur, selenium, and tellurium have atomic numbers of 16, 34, and 52, respectively, thus showing that the atomic number of the middle of these three

Summary of How the Elements as Basic Substances are Regarded by Various Authors.

Bent and Weinhold	Neutral atoms
Schwarz	Bonded atoms
Mendeleev, Paneth, Scerri	Macroscopic elements, characterized by Z

the use of atomic numbers, and more specifically atomic number triads, may cast new light on the question of the placement of hydrogen in the periodic table [44]. This element is traditionally placed at the head of the alkali metals, with the result that it does not form part of an atomic number triad. If it is moved to the top of the halogen group, one thereby obtains a new atomic number triad consisting of H (1), F (9), and Cl (17).

Similarly, the desire to maximize the number of atomic number triads would suggest that helium should not be moved away from its traditional place at the top of the noble gases as has been suggested by proponents of the left-step periodic table such as Bent and Weinhold.

Finally, if there is any validity in the use of the triad principle in resolving such issues, it would suggest that just one criterion, Z , can be used for both primary and secondary classification. This Z can be used for primary classification, or to provide an ordering of the elements, which is of course completely uncontroversial. The new idea lies in using a relationship among values of Z (atomic number triads), to classify elements into groups or secondary classification as we are calling it here. In addition, such an approach lends further support to the notion that group 3 of the periodic table should consist of the elements Sc, Y, Lu, Lr, rather than Sc, Y, La, Ac, as one finds in many modern periodic tables. Whereas the elements Y, Lu, Lr form an atomic number triad, Y, La, and Ac do not.¹⁵

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References

1. Bensaude-Vincent, B. *Brit J Hist Sci* 1986, 19, 3.
2. Earley, J. *Found Chem* 2005, 7, 85.
3. Hendry, R. F. *Found Chem* 2005, 7, 31.
4. Scerri, E. R. *Hyle* 2005, 11, 127.
5. Sharlow, M. *Found Chem* 2006, 8, 225.
6. Bent, H. A. *New Ideas in Chemistry from Fresh Energy for the Periodic Law*; AuthorHouse: Bloomington, IN, 2006.
7. Schwarz, W. H. E. *Found Chem* 2007, 9, 139.
8. Paneth, F. A. *Brit J Philos Sci* 1962, 13, 1, and 144 [reprinted in *Found Chem* 2003, 5, 113].

¹⁵Many textbooks and even IUPAC place La and Ac in the latter positions, whereas there are good physical arguments for placing Lu and Lr in these places as argued sometime ago by Jensen [45].

9. Stroker, E. *Angew Chem Int Ed Engl* 1968, 7, 718.
10. Lavoisier, A. *Elements of Chemistry* (translated by Kerr, R.); Dover: Mineola, New York, 1965.
11. Hendry, R. F. *Stud Hist Philos Sci* 2006, 37, 322.
12. Mendeleev, D. I. *The Principles of Chemistry*; Longmans, Green and Co: London, 1981.
13. Mendeleev, D. I. *The Principles of Chemistry*, Vol. I (first English translation from the Russian 5th edition, translated by Kemensky, G.); Collier: New York, 1891; p 23.
14. Soddy, F. *The Chemistry of the Radio-Elements*, part 1; Longmans, Green & Co.: London, 1914.
15. Crookes, W. *Reports of the British Association for the Advancement of Science*, 1886, p 558.
16. Van Tiggelen, B. In *Chemical Sciences in the 20th Century*; Reinhardt, C., Hoffmann, R. Eds.; Wiley-VCH, 2001; p 131.
17. Scerri, E. R. In *Of Minds and Molecules*, Bhushan, N.; Rosenfeld, S., Eds.; Oxford University Press: New York, 2000, p 51.
18. Scerri, E. R. *The Periodic Table, Its Story and Its Significance*; Oxford University Press: New York, 2007.
19. Gross, P. R.; Levitt, N. *Higher Superstition*; Johns Hopkins University Press: Baltimore, 1994.
20. Sokal, A. *Social Text* 1996, 46, 217.
21. Bent, H. A.; Weinhold, F. *J Chem Educ* 2007, 84, 1145. Available at www.jce.divched.org/Journal/Issues/2007/Jul/jceSubscriber/JCESupp/JCE2007p1145W.pdf.
22. Schwartz, A. T. *J Chem Educ* 2007, 84, 1431.
23. Janet, C. *Chem News* 1929, 138, 372.
24. Löwdin, P.-O. *Int J Quantum Chem* 1969, S3, 331.
25. Allen, L. C.; Knight, E. T. *Int J Quantum Chem* 2000, 90, 80.
26. Scerri, E. R. *Found Chem* 2006, 8, 285.
27. Scerri, E. R. *Stud Hist Philos Sci* 2006, 37, 308.
28. Ostrovky, V. N. *Found Chem* 2001, 3, 145.
29. Scerri, E. R. *Am Sci* 1997, 85, 546.
30. Scerri, E. R. *Found Chem* 2004, 6, 93.
31. Vanquickenborne, L. G.; Pierloot, K.; Devoghel, D. *J Chem Educ* 1994, 71, 469.
32. Mendeleev, D. *Rev Gen Chim Pur Appl* 1899, 1, 211; Translated in *Mendeleev on the Periodic Law, Selected Writings, 1869–1905*, Ed. Jensen, W. B., Dover: Mineola, New York, 2002.
33. Paneth, F. A. In *Chemistry and Beyond*; Dingle, H., Martin, G. R., Eds.; Wiley: New York, 1965; p 53.
34. Schwarz, W. H. E. In *Fundamental World of Quantum Chemistry: A Tribute to Per-Olov Löwdin*, Vol. 3; Brandas, E., Kryachko, E. S., Eds.; Springer: Dordrecht, 2004; p 645.
35. Dobereiner, W. *Ann Phys Chem (Poggendorf)* 1829, 15, 301.
36. Atkins, P. W.; Kaesz, H. *Chem Int* 2003, 25, 14.
37. Cronyn, M. W. *J Chem Educ* 2003, 80, 947.
38. Dash, H. H. *Nature* 1963, 198, 25.
39. Dash, H. H. *Nature* 1964, 202, 1001.
40. Sacks, L. J. *Found Chem* 2006, 8, 31.
41. Boeyens, J. C. A. *J Radio Nucl Chem* 2003, 257, 33.
42. Boeyens, J. C. A.; Levendis, D. C. *Number Theory and the Periodicity of Matter*; Springer: Dordrecht, 2008.
43. Bonchev, D.; Kamenska, V. *J Phys Chem* 1981, 85, 1177.
44. Scerri, E. R. *J Chem Educ* 2008, 85, 585.
45. Jensen, W. B. *J Chem Edu* 1982, 59, 634.