

Introduction

My interest in the periodic table has at least two aspects. Firstly, like so many people before me, I fell in love with the rational beauty of the periodic chart that appears to systematize all the kinds of elementary substances that a student of chemistry would ever encounter.¹ The extent to which students are exposed to the periodic table and the stage at which this takes place seems to vary a good deal depending on geographical location and on the era in which they learn chemistry. In my own case it was in London in the 1960s where we were not initially taught the periodic table, although it was displayed on the classroom walls.

The first time I recall being clearly directed to the periodic table and some of its features, was on making the transition between Ordinary Level and Advanced Level chemistry at age 16. This delay added to the delight of the discovery, if anything, since I experienced the wonder of seeing how previously covered information suddenly fell into place in a coherent framework.

Unlike some lovers of the periodic table, I am not somebody who played with chemicals or minerals at a young age. My attraction to the periodic table was more in the realm of ideas. It is not too surprising looking back now that I should have ended up with an interest in history and philosophy of chemistry.²

My second interest in the periodic table arose much later when I became a PhD student in history and philosophy of science working on the question of the reduction of chemistry to quantum mechanics. First of all, the periodic table serves as an excellent arena in which to pose this question in a more restricted form than asking whether all of chemistry reduces to quantum mechanics. Secondly, the periodic table and the attempts to understand it theoretically were directly responsible for several developments in theoretical physics which contributed to the development of quantum mechanics. For example, Thomson's model of the atom, whereby electrons circulated in rings within the positive charge, provided the earliest forms of the ubiquitous electronic configurations, which these days occur throughout chemistry and physics. Bohr's model of the atom was guided and motivated by trying to understand the periodic table, as was the postulation of a fourth quantum number by Pauli and the subsequent discovery of electron spin.

¹Or anyone for that matter, although these days there is a good deal of talk of "dark matter" which is not featured on the periodic table.

²E. R. Scerri, *Collected Papers on Philosophy of Chemistry*, Imperial College Press, London, 2008.

The papers in this volume are presented in chronological order in which they were written, rather than being arranged thematically. They begin with material written while I was completing my PhD thesis at King's College, London and they deal primarily with the question of reduction. However, the first two papers are directed at different audiences and so take up different aspects of the question of reduction.

For chemists, and chemical educators especially, there is an area of ongoing debate concerning the periodic table. Some educators regard the periodic table as being primarily about the macroscopic elements and their properties. They typically begin by pointing out the variety among the elements and the striking similarities displayed between some of the elements. This approach tends to be macroscopic, following the historical development of the periodic system and the fact that the system was discovered well before the advent of modern atomic theory and quantum mechanics.³

The second approach, and far more common these days, lies in starting with current knowledge and placing the emphasis on a microscopic account. Atomic theory, electronic configurations, electron shells and orbitals are put to the fore with the view that these concepts represent the fundamental basis for chemistry and should therefore come first. The periodic table thereby glides effortlessly from being a table of the elements to being a table of the atoms. What students are deprived of in this approach is the delight that I and many others discovered as students, in seeing the periodic table as a means of unifying a large number of previously encountered chemical facts. Students who encounter the fundamental principles first, simply don't have much information that is in need of unification. Then there is the deeper question of whether the supposedly more fundamental quantum description really does the job that it is claimed to do. But more on this further question a little later. Let me now return to the papers in this volume.

In an article that first appeared in the *Journal of Chemical Education*, I considered the relationship, or perhaps the tension, between the periodic table of the elements arranged according to chemical properties and the periodic table of the atoms coming largely from the field of physics. This is a subject that continues to be at the center of my interests, although I have changed my mind on a number of issues as these papers will show.

For example, in this early paper I considered the Janet or left-step table but quickly dismissed it in spite of its esthetic beauty and apparent coherence with the quantum mechanical account of the periodic table. The left-step periodic table consists of moving the s block elements to the right flank of the periodic table, thereby displaying the blocks in what is perhaps a more logical order of f, d, p and s blocks, reading from left to right, rather than the sequence of s, d, p as one sees in the medium-long form or even s, f, d, p in the long-form table.

This much is quite readily acceptable but proponents of the left-step table make an additional change to the conventional format by moving the element helium from the head of the noble gases to the head of the alkaline earths. Given my initial preference for purely

³Dalton's work, published in the early 1800s, of course precedes the birth of the periodic system which mostly took place in the second half of the 1800s.

chemical arguments over those based primarily on atomic physics and quantum mechanics, I initially sided with the chemists in claiming that helium should not be moved in this manner.⁴ After my brief conversion to the left-step table, which took place in the early single digit years, I reverted again to this more traditional, or chemical view, of leaving helium among the noble gases.⁵

Another issue raised in this first paper is that of the elements which should be placed in group 3 of the periodic table. At this time, the paper by William Jensen advocating Sc, Y, Lu, Lr appeared to be quite compelling to me. I believe that I subsequently convinced a number of textbook authors to switch to this grouping rather than the more customary Sc, Y, La, Ac. It came as something of a surprise to me, some years later, to discover that the arrangement advocated by Jensen was being questioned and that some authors were advocating a return to group 3 as Sc, Y, La and Ac. One of these traditionalists is my friend and UCLA colleague Laurence Lavelle, who subsequently published a commentary in the *Journal of Chemical Education* in which he reiterated the traditional grouping for group 3.⁶

Still on the first article in this volume, I also discussed Seaborg's extension of the periodic table and his creation of a completely new series that he termed the actinides. I have long been interested in the genesis of this idea and even had the pleasure of putting this question to Seaborg in the late 1990s.⁷ In recent years it has become clearer to me that Seaborg's idea was not quite as original as he implied in his writings and that it is contained in many earlier periodic tables. I believe that more historical work on this question might lead to an interesting story.

One final comment on this first paper is that I recommended the use of many tables and suggested that no one table was better than others. This is something that I no longer believe. According to a realistic interpretation, the periodic system is referring to some objective relationship among the elements that exists in nature and is not the result of mere human construction. I believe that it *does* therefore make perfect sense to be seeking an optimal periodic system in the sense of one that most closely reveals the precise periodic relationship between as many elements as possible.⁸

The second paper first appeared in the *British Journal for the Philosophy of Science*. The emphasis here is naturally more philosophical and considers such questions as the

⁴As will become clear from later parts of this introduction and from the papers themselves, my views on this issue have gone full-circle and I am currently back supporting the placement of helium among the noble gases after flirting with the possibility of placing helium among the alkaline earths.

⁵I thank my UCLA colleague Herb Kaesz as well as Octavio Novarro for my returning to the view of He among the noble gases. As both of them reminded me, whereas the promotion of 2s electrons into the 2p orbitals can readily take place in beryllium, the promotion of a 1s electron into a 2s orbital in helium is highly improbable, if not completely out of the question, in view of the far larger energetic gap in this case.

⁶I have submitted a response to Lavelle's commentary which contains what I believe to be a conclusive argument in favor of the grouping of Sc, Y, Lu and Lr.

⁷I asked Seaborg this question after a talk that he gave at an ACS meeting in Las Vegas whereupon he asked me and Carmen Giunta to join him for lunch at a local diner. Although he did not really cast any light on my question but it still was a memorable occasion for Carmen and myself.

⁸This theme is resumed in several later papers in this volume.

nature of models and whether the atomic orbital model, in particular, reduces legitimately to quantum mechanics. I also attempted to trace the historical development of this model which serves as one of the central paradigms of modern chemistry.

Starting with Bohr's version of 1913, the evolution of this model was examined in an attempt to highlight the assumptions and approximations that were made at each stage. As in the case of many other papers in this volume, there is an educational motivation for raising these questions, especially in view of the central role of the atomic orbital model at all levels of chemical education. My suspicion is that many chemical educators do not appreciate the extent to which this model is an approximation and the conditions under which it ceases to be applicable.

These days students are presented with the four quantum number description of electrons in many-electron atoms as though these quantum numbers somehow drop out of quantum mechanics in a seamless manner. In fact, they do not and furthermore they emerged, one at a time, beginning with Bohr's use of just one quantum number and culminating with Pauli's introduction of the fourth quantum number and his associated Exclusion Principle.

To return to the philosophical aspects, and with the benefit of hindsight, I would now say that I took a somewhat hard-line approach to the matter in concluding that there was something of a clash between the atomic orbital model and the theory from which it is generally supposed to be derived. This view was softened in subsequent papers⁹ but I still believe that it is useful to examine the gulf between the model and the fundamental theory as clearly as possible, especially given the interest in models that has swept through philosophy of science in recent years, and just to repeat myself a little, because of the educational currency of this particular model.

In case the general reader might be wondering about the connection between atomic orbitals and the periodic table, let me address this issue briefly. As mentioned above, in the case of the first paper, the modern explanation for the periodic table is based entirely on the orbital model. It is only by ignoring the approximate nature of the model that the explanation for the periodic system might appear to be full and complete.

The third paper addresses the topic of the periodic table more directly. It appeared in 1997 in the semi-popular magazine, *American Scientist*, during the year celebrating the one hundredth anniversary of the discovery of the electron. Not only did J.J. Thomson discover the first subatomic particle, but he also set about trying to explain the periodic table by means of arrangements of electrons within his plum pudding model of the atom. This was an atomic model in which electrons were regarded as being embedded within the positive charge throughout the atom, like plums in a pudding.

Moreover, Thomson considered that the electrons rotated within the positive charge in the form of concentric rings, an idea which he adopted on reading about Alfred Meyer's

⁹E. R. Scerri, Normative and Descriptive Philosophy of Science and the Role of Chemistry, in *Philosophy of Chemistry, the Synthesis of a New Discipline*, D. Baird, E. R. Scerri, L. McIntyre (eds.), Boston Studies in the Philosophy of Science, Vol. 242, pp. 119–128, 2005; E. R. Scerri, Philosophy of Chemistry — A New Interdisciplinary Field? *Journal of Chemical Education* 77: 522–526, 2000.

experiments with steel needles floating on corks in a basin of water. So it emerges that today's ubiquitous notion of electronic structure originated in a classical mechanical context and did not have to wait for the advent of Niels Bohr or any other quantum mechanicians. In fact, Niels Bohr's even more famous atomic model, with electrons in quantized orbits, arose in direct response to Thomson's model. Bohr was at the time a postdoctoral fellow in the UK, where he divided his time between Thomson in Cambridge and Rutherford, whom he found far more congenial, in Manchester.

In my paper I argue that as atomic orbits morphed into non-deterministic atomic orbitals in the fully quantum mechanical theory of Schrödinger and Heisenberg, so they became regarded instrumentally rather than realistically. Within a quantum mechanical context, orbitals cease to be real in that they cease to exist as referring entities. How ironic then that a mere two years later a team of chemists and physicists should have made front page news in *Nature* magazine by claiming that orbitals had been directly observed for the first time!¹⁰

This was a claim that I and several other authors criticized in a number of journals, but unfortunately not in *Nature* magazine.¹¹ Although the authors of the "Orbitals Observed" study protested their innocence, it became clear that their claims had been incorrect and exaggerated.¹² In a section of the same paper, I discussed the notion that the 4s atomic orbital is occupied "before" the 3d orbitals. This has subsequently turned out to be incorrect and there is conclusive spectroscopic evidence to the contrary which seemed to have escaped the attention of several authors who have written on this issue, including myself.¹³

Paper four first appeared in the *Journal of Chemical Education* and aimed to highlight one of the important ways in which the periodic table is not fully explained by quantum mechanics. The orbital model and the four quantum number description of electrons, as described earlier, is generally taken as the explanation of the periodic table but there is an important and often neglected limitation in this explanation. This is the fact that the possible combinations of four quantum numbers, which are strictly deduced from the theory, explain the closing of electron shells but not the closing of the periods. That is to say the deductive explanation only shows why successive electron shells can contain 2, 8, 18 and 32 electrons respectively.

¹⁰J. M. Zuo, M. Kim, M. O'Keefe, J. H. C. Spence, Direct Observation of d-Orbital Holes and Cu-Cu Bonding, *Nature* 401: 49–52, 1999; C. J. Humphreys, Electrons Seen in Orbit, *Nature* 401: 21–22 1999.

¹¹P. Coppens, *International Union of Crystallography Newsletter*, 8: 4, 2000; E. R. Scerri, Have Orbitals Really Been Observed? *Journal of Chemical Education*, 77: 1492–1494, 2000; E. R. Scerri, N. Koertge, ed. *The Recently Claimed Observation of Atomic Orbitals and Some Related Philosophical Issues*, *Philosophy of Science*, 68: S76–S88, 2001; S. Wang, W. H. E. Schwarz, On Closed-Shell Interactions, Polar Covalences, d Shell Holes, and Direct Images of Orbitals: The Case of Cuprite, *Angewandte Chemie International Edition*, 39: 1757–1762, 2000. Although a number of authors including Coppens, Schwarz and myself wrote to the editor of *Nature* magazine, no letters of dissent were accepted.

¹²If the announcement was designed to attract the notice of the scientific press, it did just that. For example, M., Jacoby, Picture Perfect Orbitals, *Chemical & Engineering News*, 77: 8, 1999.

¹³F. L. Pilar, 4s Is Always Above 3d! Or, How to Tell the Orbitals From the Wavefunctions, *Journal of Chemical Education*, 55: 2–6, 1978; E. R. Scerri, M. Melrose, Why the 4s Orbital Is Occupied Before the 3d, *Journal of Chemical Education*, 73(6): 498–503, 1996; L. G. Vanquickenborne, K. Pierloot, D. Devoghel, Transition Metals and the Aufbau Principle, *Journal of Chemical Education*, 71: 469–471, 1994.

However, this feature alone does not fully explain the form of the periodic table. It is rather the question of the closing of periods which any candidate explanation must provide. But the latter is only available in a semi-empirical form at present. The reason why this additional requirement often seems to go unnoticed lies in something of a coincidence as I try to explain in the article. While the closing of shells occurs after particular numbers of electrons have been added, if one now considers cumulative totals, namely 2, 10, 28, 60 etc., many of these values do not coincide with the atomic numbers representing the closing of periods. In fact the periods close at the atomic numbers of 2, 10, 18, 36, 54 etc., and the discrepancy occurs because electron shells do not fill sequentially. In other words, the filling of electron shells does not proceed according to increasing values of the n quantum number but instead according to increasing $n + \ell$, or according to the Madelung rule as it is sometimes called.

Another aspect of this state of affairs is that all periods repeat once, with the exception of the first period of just two elements, to produce the sequence of 2, 8, 8, 18, 18, 32, etc. The focus of interest thus turns to whether the Madelung rule itself can be strictly deduced from theory, a theme that is taken up in later papers in this collection.

The following paper, the fifth one, marks something of a shift in emphasis. In a long paper co-authored with John Worrall from the London School of Economics (LSE), we set out to examine just how important predictions were in the acceptance of the periodic table by the scientific community of the late 1800s. This question has nothing to do with quantum mechanics which did not exist until 1905, even if one just considers the very early work of Max Planck.

Let me say a little by way of background. I first learned of this issue while writing my PhD thesis at King's College, London from a fellow graduate student who had some connections with the LSE. On reading Worrall's papers I found that there was a long-standing debate over the question of whether successful predictions are more influential than so-called accommodations (explaining already known facts) when scientists come to accept a new theory. The commonplace view is of course that predictions matter more, for the simple reason that in the case of predictions there can be no suspicion that the creator of the new theory might have doctored the theory to explain the facts. The facts were simply not known when the theory was created.

I was also familiar with the work of science historian Stephen Brush who had argued that in most important cases, such as relativity theory and quantum mechanics, and contrary to popular opinion, it was successful accommodations that had swayed scientists of the time rather than any dramatic predictions.

Worrall had made similar claims regarding theories of light developed in the seventeenth century and in particular, the case of Fresnel whose dramatic and subsequently confirmed predictions had not been as influential as his accommodation of already known optical phenomena. Meanwhile, Stephen Brush had turned his attention to chemistry and the periodic table, given that this seemed to be a case for which successful predictions made by Mendeleev are widely held to have been the reason for the acceptance of the periodic

table. Rather surprisingly, to my mind, Brush was claiming that perhaps the periodic table represented one important exception.¹⁴ In this case Brush claimed that successful predictions *had been* the deciding factor in the acceptance of the periodic system.

I published a short paper in a somewhat obscure conference proceedings in which I disagreed with Brush.¹⁵ I then approached Worrall to see if he wanted to team-up with me to take a closer look at the issue. At first he did not seem too interested but this changed after I became a post-doctoral fellow at the LSE and continued to press Worrall to work on this project.

The result of our eventual collaboration is reprinted here. To state our conclusion briefly, we argue that it is not the temporal aspect that is important but rather the question of whether a scientist uses known facts to develop his or her theory (use-novelty). Such use-novelty had been previously discussed by Imre Lakatos and his then graduate students Elie Zahar and none other than John Worrall.¹⁶

In the paper under discussion, which has subsequently been cited by a number of authors,¹⁷ Worrall and I argue that Mendeleev's ability to literally *accommodate* something like 60 elements into the periodic system, subject to a number of constraints, contributed at least as much, if not more, to the acceptance of the periodic table than did Mendeleev's famous successful predictions.

The sixth article in this collection takes up the story from where paper 4 left off. If the $n + \ell$ (Madelung) rule can be fully reduced, then it might rightly be claimed that the periodic table reduces fully to quantum mechanics. This is a question that has been asked in a much-quoted paper by Per-Olov Löwdin, the influential quantum chemist who for many years led the Quantum Chemistry project at the University of Florida.

The paper resulted from an invitation to contribute to what eventually became a three-volume dedication to the memory of Löwdin. In addition to addressing the question of whether the $n + \ell$ rule has been derived, I used this opportunity to explore the reduction of the periodic table in more general terms.

The term *ab initio* is often used in theoretical chemistry and even in the general chemistry literature. In the paper I try to explore precisely what this term means. Does it really refer to calculations carried out from first principles without any recourse whatsoever to empirical data? Surprisingly, I found that theoretical and computational chemists use this term with

¹⁴S. J. Brush, Prediction and Theory Evaluation, *Science*, 246: 1124–1129, 1989.

¹⁵E. R. Scerri, Stephen Brush, the Periodic Table and the Nature of Chemistry, in *Die Sprache der Chemie*, P. Jannich, N. Psarros (eds.), pp. 169–176, 1996.

¹⁶It was Zahar who first pointed out to Lakatos the importance of some forms of accommodation, or what was later termed use-novelty. Refer to Lakatos and Zahar, *The Methodology of Scientific Research Programmes: Philosophical Papers* by Imre Lakatos, John Worrall, Gregory Currie, CUP, 1980.

¹⁷E. Barnes, On Mendeleev's Predictions: Comment on Scerri and Worrall, *Studies in History and Philosophy of Science*, Part A, 36: 801–812, 2005; S. Schindler, Use-novel predictions and Mendeleev's Periodic Table: Response to Scerri and Worrall, *Studies in History and Philosophy of Science*, Part A, 39: 265–269, 2008; D. Harker, On the Predictions for Predictions, *British Journal for the Philosophy of Science*, 59: 429–453, 2008; E. R. Scerri, Response to Barnes' Critique of Scerri and Worrall, *Studies in History and Philosophy of Science*, 36: 813–816, 2005.

a variety of different meanings. And none of these meanings seem to demand calculations with no experimental input whatsoever.¹⁸

My article also considers different levels of explanation for the periodic table using increasingly sophisticated approaches. The most elementary explanation of chemical periodicity lies of course in the notion that members of a group of elements share the same number of outer-shell electrons. But this simple model is an approximation. If calculations are carried out on the assumption that atoms possess just their ground state configurations, the predictions obtained are highly inaccurate. Another explanation for the periodic table, already touched on in other papers, lies in the possible combination of quantum numbers. The highest-level explanations abandon the static idea of one arrangement of electrons in a particular set of orbitals, or rather they use the notion as a first level approximation to be augmented by thousands or even millions of contributions from other configurations. But these approaches use basis sets, which are experimentally derived and so not entirely *ab initio* in the pure sense of the term. Finally, the paper discusses more sophisticated approaches such as density functional methods, which offer the promise of a universal solution but which invariably resort to the form of empirical mathematics whereby the Schrödinger equation for every atom must be solved separately.

Paper seven is of a more general nature and again more about the history of chemistry than about the role of quantum mechanics. As in the case of my book on the periodic table, this article was written in commemoration of the one hundredth anniversary of the death of Mendeleev in 1907.¹⁹ The article reviews the many precursors to Mendeleev's discovery including the work of Döbereiner, De Chancourtois, Newlands, Odling, Hinrichs and Lothar Meyer. With the exception of Döbereiner who discovered triads of elements, all the others published coherent periodic tables before Mendeleev's first table of 1869. The article discusses the philosophical distinction between elements as "basic substances" and elements as "simple substances" and the use to which this distinction was put by Paneth at the beginning of the twentieth century following the apparent threat to the periodic system which occurred when so many new isotopes were discovered. The article continues by summarizing the way in which the discovery of the electron provided the key to a deeper understanding of the periodic system through the researches of Thomson, Bohr, Pauli and many others. Finally, alternative forms of the periodic table are discussed including those proposed by Janet, Stewart and Benfey.

Paper eight first appeared in the *Journal of Chemical Education* in 2008. Whereas in my book on the periodic table, I recommended the left-step table as the best possible representation, I subsequently changed my mind and proposed a new table. First of all let me say why I initially supported the left-step table. My attention was first drawn to the left-step table by Henry Bent's unpublished booklets on the subject, although I felt that his

¹⁸Of course I exclude the need to derive fundamental constants.

¹⁹The article began life as an invited talk at the Chemical Heritage Foundation in Philadelphia and was followed by an article in the foundation's magazine, *Chemical Heritage*.

arguments were too partisan, too numerous and that some stretched the reader's credulity a little too far.

What actually converted me to the left-step table, at least for a period of a few years, was a rather concise paper by the periodic table designer Gary Katz, which appeared in *The Chemical Educator*.²⁰ My own support for this form of the table centered on my interest in the dual sense of the term "element" and in particular the more fundamental sense, called element as a "basic substance" by Paneth.

But I am getting ahead of myself. Let me first say what I see as the advantages of this representation. Instead of confining the s-block of elements to the left side of the table where it looks a little out of place, the left-step table moves the s-block to the right hand edge of the table. This produces a pleasing and seemingly more natural sequence in the main blocks of the periodic table. Whereas in the convention of medium-long form table these blocks appear in the order s, d, p with the f block as a kind of footnote, in the left-step table one has the order of f, d, p and s reading from left to right. Moreover, the element helium is removed from its usual place at the head of the noble gases and placed instead at the head of the alkaline earth elements on the basis of its s^2 electronic configuration that is shared by these metals.

As a result of these two changes, the left-step table removes a rather annoying blemish from the conventional periodic table. It has been a source of puzzlement to many authors as to why the first short period of two elements does not repeat in the same way that the other period lengths repeat (8,8,18,18,32, and presumably 32). In the left-step table, the first very short period consisting of two elements *does* repeat. In addition, the order of orbital filling appears to be better reflected in the left-step table as mentioned earlier in this introduction. In the conventional or medium-long table or even the long-form table, there is an important sense in which these tables are predicated on the false notion that orbital filling takes place according to increasing values of the main quantum number n . The order of filling does not follow this order but to a good approximation obeys a rule on increasing $n + \ell$, the Madelung rule. In the left-step table, each distinct period reflects a particular value of $n + \ell$ and not n . Finally, although this may be somewhat of a cosmetic feature, there are no gaps such as between Be and B or Mg and Al in the left-step table as one finds in the conventional table format.

With all these advantages one might well wonder why the left-step table has not attracted more attention and indeed why it has not been widely adopted. The answer to this question lies in the placement of one crucial element, helium. In the left-step table, helium is placed among the alkaline earth metals as mentioned above. To most chemists this is completely abhorrent since helium is regarded as the noble gas *par excellence*. Meanwhile, to a physicist or somebody who emphasizes electronic properties, helium falls rather naturally into the alkaline earths since it has two outer-shell electrons.

²⁰G. Katz, The Periodic Table: An Eight Period Table for the 21st Century, *The Chemical Educator*, 6: 324–332, 2001.

Here then is an interesting case of the clash between chemistry and physics, an example, which highlights the importance of the question of the reduction of chemistry. Should one follow chemical intuition in resisting the evidence from electronic configurations and the suggestive nature of the left-step table? Or should one follow the reductionist approach in insisting that helium is an alkaline earth in the belief that it might eventually even show chemical similarities to the alkaline earths? These are the standard arguments for and against the left-step table.

What I hope to have added to the discussion has been a philosophical reflection on the nature of the concept of “element” and in particular an emphasis on elements in the sense of basic substances rather than just simple substances. The view of elements as basic substances, is one with a long history. The term is due to Fritz Paneth, the prominent twentieth century radio-chemist. This sense of the term element refers to the underlying reality that supports element-hood or is prior to the more familiar sense of an element as a simple substance. Elements as basic substances are said to have no properties as such although they act as the bearers of properties. I suppose one can think of it as a substratum for the elements. Moreover, as Paneth and before him Mendeleev among others stressed, it is elements as basic substances rather than as simple substances that are summarized by the periodic table of the elements. This notion can easily be appreciated when it is realized that carbon, for example, occurs in three main allotropes of diamond, graphite and buckminsterfullerenes. But the element carbon, which takes its place in the periodic system, is none of these three simple substances but the more abstract concept of carbon as a basic substance.

It occurred to me that if one concentrated on this more fundamental sense of the concept of element, then the fact that helium does not seem to have properties in common with the alkaline earths would not be sufficient reason for not placing it among these elements in the periodic table. As I have later described this position, it was a form of “why not argument” rather than a positive reason for why helium *should* be placed among the alkaline earths.

Then came my change of mind. Rather than relying on such a convoluted justification for the placement of helium among the alkaline earths, and having failed to convince a large number of colleagues of the view that helium belongs with the alkaline earths, I decided to return to my original anti-reductionist point of view and to insist, like most chemists, that helium must remain among the noble gases despite its s^2 configuration. However, I also suggested the repositioning of another element for reasons which I believe have not been previously considered.

I became increasingly interested in triads of elements, partly because of their historical importance. As I claimed in my book, the discovery of atomic weight triads represents the first major hint that there exists some regularity that underlies the elements.²¹ Triads represent the first hint of a systematic and quantitative foundation between the numerical properties of the elements. Now since atomic weight was replaced by atomic number, it is

²¹E. R. Scerri, *The Periodic System, Its Story and Its Significance*, Oxford University Press, New York, p. 179, 2007.

natural to consider atomic number triads. With the exception of a single obscure paper published in the 1930s, nobody had paid much attention to atomic number triads.²² Unlike atomic weight triads, these modern versions are exact in about 50% of all possible triads among the elements in the periodic system. For example, Li, Na and K form a perfect atomic number triad, $[(3 + 19)/2 = 11]$, whereas Na, K and Rb do not even do so approximately $[(11 + 37)/2 = 24 \neq 19]$.

I wondered whether there might be some means of maximizing the number of atomic number triads that appear on the periodic table. One thing was immediately clear, namely that the relocation of helium, as proponents of the left-step favor, would lead to the *loss* rather than the gain of an atomic number triad. This was therefore one more argument against the relocation of helium.

On the other hand, the relocation of hydrogen, helium's traditional partner in the first very short period, would produce a new atomic number triad if hydrogen were moved to the halogen group. $[H(1) + Cl(17)/2 = F(9)]$. So rather than moving helium from right to left in the periodic table, I proposed moving hydrogen from left to right.

Paper nine is another one that appeared in *American Scientist*. In it I took a philosophical look at two important ideas that contributed to the evolution of the periodic system. These two ideas are Prout's hypothesis and the notion of triads, which was the subject of paper eight. Both hypotheses are interesting because they were extremely productive even though they both turned out to be refuted some time later. The fact that this should happen lends some support to the views of Karl Popper who always claimed that refutability was the all important aspect of good hypotheses and theories and not whether they turn out to be correct or not.²³ For Popper, all that we really have is tentative theories and not theories that last forever.

The final paper in this collection is very recent and appeared in the *International Journal of Quantum Chemistry* where articles on Madelung's rule have previously been published. It was in this journal that its founder Per Olov Löwdin first drew attention to the fact that the rule had not yet been derived from quantum mechanics.²⁴ More recently Allen and Knight published what they claimed provided just such a long-awaited derivation.²⁵

My own paper addresses various attempts to derive the Madelung rule, including that of Allen and Knight as well as a more recent attempt by Bent and Weinhold.²⁶ But I believe my paper also breaks new ground by discussing whether there is any need at all to derive the Madelung rule, a notion which I thank Eugen Schwarz for first drawing my attention to. In addition to Madelung's rule, the paper examines all the recent themes that I think are

²²J. P. Montgomery, Döbereiner's Triads and Atomic Numbers, *Journal of Chemical Education*, 8: 162–162, 1931.

²³This is actually the pessimistic meta-induction associated with Larry Laudan among other philosophers. L. Laudan, A Confutation of Convergent Realism, *Philosophy of Science*, 48: 1–49, 1981.

²⁴P.-O. Löwdin, Some Comments on the Periodic System of the Elements, *International Journal of Quantum Chemistry, (Symposium)* IHS, 331–334, 1969.

²⁵L. C. Allen, E. T. Knight, The Löwdin Challenge, *International Journal of Quantum Chemistry*, 90: 80–88, 2000.

²⁶H. A. Bent, F. Weinhold, News from the Periodic Table: An Introduction to Periodicity Symbols, Tables, and Models for Higher-Order Valency and Donor–Acceptor Kinships, *Journal of Chemical Education*, 84: 1145, 2007.

important in the study of the foundations of the periodic table, including the dual nature of the concept of an element and whether or not an optimal form of the periodic system might exist. I carry out an analysis of the recent work of Schwarz who has been one of the few chemists to take seriously the distinction between an element as a basic substance and as a simple substance.²⁷

Schwarz also makes the interesting identification between neutral atoms and elements as simple substances on one hand, and between bonded atoms and elements as basic substances on the other hand. As a frequent participant at conferences on the philosophy of chemistry, Schwarz seems to have fully grasped the importance of this distinction between the two senses of the macroscopic element. Whether or not his one-to-one identification of the dual sense of an “element” with microscopic atoms is meaningful remains to be seen, but here I argue that he is mistaken.

Schwarz uses his understanding of the situation to suggest that all the recent attention on the Madelung rule is misplaced. He argues that if the periodic system is fundamentally a classification of the elements as basic substances, then it should also be regarded as a classification of bonded atoms rather than of neutral isolated atoms. Consequently he believes that one should concentrate on an orbital filling rule that applies to bonded atoms or ions. Such a rule is that orbitals are filled in order of increasing main quantum number n and not the more complicated Madelung rule of increasing $n + \ell$.

To take this idea seriously would require that we abandon the familiar table of isolated atoms and begin to think about how to set up a table of bonded atoms of the elements. Schwarz does not actually carry out this further step in his own writing. In my own paper, which is reproduced in this collection, I try to build such a table and quickly arrive at the conclusion that the idea is un-workable since it cannot be carried out categorically.

Instead I propose a more radical solution, namely that of *not* identifying bonded atoms with elements as basic substances, a view for which I claim support from the work of Mendeleev and Paneth. This does not solve the problem of redesigning a periodic table to reflect the behavior of bonded atoms. But if we are to retain the traditional periodic table of neutral atoms, we may still forge a connection with elements as “basic substances” by arranging the elements so as to maximize atomic number triads, where atomic number may now be interpreted to also mean “element number”.

²⁷W. H. E. Schwarz, Towards a Physical Explanation of the Periodic Table (PT) of Chemical Elements, in *Fundamental World of Quantum Chemistry: A Tribute to Per-Olov Löwdin*, Vol. 3, E. Brandas, E. Kryachko (eds.), Springer, Dordrecht, pp. 645–669, 2004. Also see: S.-G. Wang, W. H. E. Schwarz, Icon of Chemistry: The Periodic System of Chemical Elements in the New Century, *Angewandte Chemie International Edition*, 2009 (in press).